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Leather Tannery Waste Management Through Process Change, Reuse and Pretreatment

Pfister and Vogel Tanning Co, Milwaukee, Wis

Prepared for

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LEATHER TANNERY WASTE MANAGEMENT THROUGH PROCESS CHANGE, REUSE AND PRETREATMENT

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LEATHER TANNERY WASTE MANAGEMENT THROUGH PROCESS CHANGE, REUSE AND PRETREATMENT

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The title of this report aptly describes the contents - "Industrial Waste Water Management in Tanneries through Process Change, Reuse and Pretreatment." The authors provide details for design of a sulfide oxidation unit to treat unhairing liquor, a chrome recovery unit, a protein precipitation process and methods of water conservation. This work is a major contribution to the state of the art regarding lowering pollution loadings from tanneries. The authors worked in close harmony with the project officer and have provided many details of tannery pollution characteristics not previously recorded. Either the authors or project officer can provide further information on the subject matter contained herein.

David G. Stephan
Director
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ABSTRACT

Pfister & Vogel Tanning Company discharges process wastes to Milwaukee's Sewage Treatment/Fertilizer Manufacturing Plant. At a daily production level of 4,350 cattlehides, wastewater volume average 1.42 mgd, containing 17,300 lb BOD-5 (54,600 lb COD); and the 126,000 lb of total solids analyzed 38,500 lb of suspended solids. Total nitrogen averaged 4,070 lb. These wastes also contained 7,370 lb of Oil and Grease, 828 lb of sulfide, 14,700 lb of alkalinity, and 1,340 lb of total chromium. While the incremental pH varied from 3.3 to 12.7, composited samples averaged 9.8. Subprocess waste fractions have been characterized.

This project demonstrates pollution reductions for a large side leather tannery through process changes, recovery, reuse, and pretreatment. Traditional tanning operations were replaced by a straight-through process. Salt-cured hides, loaded dry to a hide processor (cement-mixer) are not removed until chrome tanning is completed, thereby effecting a 50% reduction in beamhouse-tanyard effluent volumes. Additional reductions in trivalent chromium, sulfides and Oil and Grease have been demonstrated. Investigations into protein recovery, and hydrocyclonic separation of solids from selected wastes have been initiated.

Work included in this report covers research on pilot and bench scale units as well as in full plant scale operation. Trivalent chromium was removed from waste streams and re-used in subsequent tanning operations. Sulfide removal was accomplished through plant scale catalytic oxidation. Oil and Grease level in the total plant effluent was reduced by process modification.

This report is submitted by Pfister & Vogel Tanning Company in fulfillment of Grant Number S-801037, under partial sponsorship of the Environmental Protection Agency. Work was completed in March 1976.

CONTENTS

Section		Page
I	Introduction	1
II	Conclusions	3
III	Recommendations	6
IV	Background	7
V	Waste Surveys	9
VI	Chrome Recovery Feasibility Studies	13
VII	Chrome Recovery System Design	70
VIII	Chrome Recovery System-Full Scale Operation	81
IX	Chrome Recycle-Matched Pairs Leather Tests	92
X	Hydrogen Sulfide Control	97
XI	Sulfide Oxidation in Unhairing Wastes-Feasibility Studies	103
XII	Sulfide Oxidation System Design	120
XIII	Sulfide Oxidation System-Full Scale Operation	133
XIV	Recovery of Crude Protein from Oxidized Unhairing Waste	146
XV	Removal of Solids from Soak Wastes	153
XVI	Generation of Oil & Grease and Chrome During Blue Stock Wringing	156
XVII	Gravity Separation of Oil & Grease from Beamhouse Wastes	159
XVIII	Recovery of Lime from Spent Lime Liquors	162
XIX	Acknowledgments	166
XX	References	167

FIGURES

Number		Page
1	Hide handling steps for traditional hair-save process. . . .	8
2	Effect of pH on supernatant chromium concentration.	18
3	Effect of Nalcolyte 677 on the settling of NaOH-precipitated chromium hydroxide.	22
4	Effect of Nalcolyte 677 on the settling of $Ca(OH)_2$ precipitated chromium hydroxide	23
5	Dissolved air flotation apparatus	26
6	Settling of lime-precipitated chromium hydroxide.	29
7	Suspended solids vs chromium for lime-precipitated chromium hydroxide.	30
8	Graphical determination of the rate of subsidence and thickener retention time	31
9	Effect of chromium concentration on design volumetric loading	37
10	Effect of suspended solids concentration on design volumetric loading	38
11	Effect of suspended solids concentration on retention time	39
12	Effect of feed suspended solids concentration on underflow concentration.	40
13	Effect of suspended solids on unit area.	41
14	Büchner funnel test apparatus.	45
15	Effect of various alkalis on the filtration of chromium hydroxide	46
16	Filter leaf test apparatus	48

Number Page

17 Effect of temperature on the filtration of lime-precipitated chromium hydroxide 58

18 Hydrocyclonic separator 66

19 Flocculation of chromium hydroxide 78

20 Chrome Recovery System 80

21 Bench-scale oxidation of sulfides in unhairing wastes. . . . 106

22 Oxidation of sulfides by paddle aeration 112

23 Determination of field transfer rates. 119

24 Determination of field transfer efficiency 125

25 Determination of mean oxygen saturation value. 126

26 Sulfide Oxidation System. 132

27 Full-scale sulfide oxidation curve. 138

28 Rate curve for full-scale sulfide oxidation 139

29 Full-scale sulfide oxidation rate curve - potassium permanganate catalyst 140

30 Titration curve for acidification of oxidized hair-burn liquor. 148

31 Effect of pH on total solids for acidification of oxidized hair-burn liquor 149

32 Effect of pH on sludge volume for acidification of oxidized hair-burn liquor 150

33 Flocculent settling of lime in relime liquor. 164

TABLES

Number Page

1 EFFECT OF PROCESS CHANGE ON WASTEWATER LOADINGS 9

2 WASTEWATER LOADINGS FOR LEATHER MANUFACTURING SUBPROCESSES 11

3 TYPICAL ANALYSIS OF CONCENTRATED SPENT CHROME 15

4 EFFECT OF NaOH DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE 17

5 EFFECT OF $Ca(OH)_2$ DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE - PART I 19

6 EFFECT OF $Ca(OH)_2$ DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE - PART II 19

7 EFFECT OF NH_4OH DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE 20

8 EFFECT OF Na_2CO_3 DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE 20

9 EFFECT OF VARYING DOSAGES OF NALCOLYTE 677 ON THE SETTLING OF LIME-PRECIPITATED CHROMIUM HYDROXIDE 24

10 CHROMIUM AND SUSPENDED SOLIDS CONCENTRATIONS FOR THE SETTLING OF LIME-PRECIPITATED CHROMIUM HYDROXIDE 34

11 SURFACE AREA REQUIREMENTS FOR THE THICKENING AND CLARIFICATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE AT VARIOUS CHROMIUM AND SUSPENDED SOLIDS CONCENTRATIONS 35

12 EFFECT OF CHANGE IN CHROMIUM CONCENTRATION ON THE VOLUMETRIC SURFACE LOADING OF A THICKENER DESIGNED TO CONCENTRATE LIME-PRECIPITATED CHROMIUM HYDROXIDE 42

13 EFFECT OF DILUTION ON SEVERAL SIGNIFICANT PARAMETERS FOR THE DESIGN OF A CHROMIUM HYDROXIDE SLUDGE THICKENER 43

14 EFFECT OF VARIOUS ALKALIS ON THE FILTRATION OF CHROMIUM HYDROXIDE 50

Number Page

15 EFFECT OF VARIOUS ALKALIS ON FILTER YIELD AND FILTRATION RATE FOR CHROMIUM HYDROXIDE 51

16 FILTER LEAF TEST RESULTS - PART I 53

17 FILTER LEAF TEST RESULTS - PART II. 54

18 EFFECT OF VARIATION IN DRUM SPEED ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE - PART I. 55

19 EFFECT OF VARIATION IN DRUM SPEED ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE - PART II 56

20 EFFECT OF VARIATION IN SUSPENDED SOLIDS CONCENTRATION ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE 59

21 EFFECT OF TEMPERATURE ON THE FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE 60

22 ACIDIFICATION OF CHROMIUM HYDROXIDE FILTER CAKE - PART I. . 61

23 ACIDIFICATION OF CHROMIUM HYDROXIDE FILTER CAKE - PART II . 61

24 PILOT-SCALE VACUUM FILTRATION OF CHROMIUM HYDROXIDE 63

25 REAPPORTIONMENT OF OIL AND GREASE DURING THE FILTRATION OF CHROMIUM HYDROXIDE 64

26 CYCLONE SEPARATION OF CALCIUM SULFATE FROM SPENT CHROME LIQUOR AT VARYING ORIFICE DIAMETERS - PART I. 68

27 CYCLONE SEPARATION OF CALCIUM SULFATE FROM SPENT CHROME LIQUOR AT VARYING ORIFICE DIAMETERS - PART II 68

28 DISTRIBUTION OF CHROMIUM IN HIDE PROCESSOR WASTES 71

29 ALTERNATIVE LEVELS OF CHROME CAPTURE. 71

30 SURFACE AREA FOR SLUDGE THICKENING - PART I 75

31 SURFACE AREA FOR SLUDGE THICKENING - PART II. 75

32 SURFACE AREA FOR SLUDGE THICKENING - PART III 75

33 FILTER AREA FOR CHROMIUM HYDROXIDE 76

34 CHROME RECOVERY SYSTEM PERFORMANCE - LIME PRECIPITATION PART I 83

Number Page

35 CHROME RECOVERY SYSTEM PERFORMANCE - LIME PRECIPITATION PART II. 85

36 CHROME RECOVERY SYSTEM PERFORMANCE - SODA ASH PRECIPITATION. 89

37 CHROME RECOVERY SYSTEM OPERATING COSTS - SODA ASH VS LIME PRECIPITATION 90

38 PROPORTIONS OF DISSOLVED SULFIDE PRESENT AS H_2S. 98

39 OXYGEN UPTAKE FOR SULFIDE OXIDATION. 109

40 SULFIDE OXIDATION BY PADDLE AERATION 111

41 EFFECT OF CATALYST DOSAGE ON SULFIDE OXIDATION BY PADDLE AERATION. 114

42 SULFIDE OXIDATION BY SURFACE AERATION - PILOT SYSTEM. 115

43 CUMULATIVE CAPTURE OF SULFIDES. 121

44 ALTERNATIVE LEVELS OF SULFIDE COLLECTION AND TREATMENT. . . . 121

45 OPERATING COSTS FOR VARIOUS SULFIDE OXIDATION METHODS 130

46 EFFECT OF CATALYST DOSAGE ON SULFIDE OXIDATION. 135

47 TREATMENT OF UNHAIRING WASTES BY PROTEIN PRECIPITATION. . . . 151

48 SIEVE ANALYSIS OF SAND FROM SOAK LIQUOR. 154

49 EFFECT OF WRINGING ON BLUE STOCK ANALYSIS. 157

50 CHROME AND FATS DISCHARGED FROM BLUE STOCK WRINGING. 158

51 EFFECT OF FLOTATION ON THE OIL AND GREASE CONTENT OF VARIOUS WASTE FRACTIONS. 161

52 FLOTATION OF PICKLE/SOAK WASTEWATER MIXTURES. 161

SECTION I

INTRODUCTION

Approximately 60% of the leather produced in the United States is tanned in plants located in municipalities(1). The combined treatment of industrial and sanitary wastes offers a more efficient reduction of industrial wastes, and minimizes duplication of treatment operations. Most municipal tanneries discharge their process wastewaters to municipal sewerage systems without extensive pretreatment. With the enactment of the Water Pollution Control Act Amendments of 1972, Publicly Owned Treatment Works (POTW's) must now establish a system of User Charges as well as a program for Industrial Cost Recovery to qualify for Construction Grants. The concentrations of pollutants in tannery wastes, as measured by BOD and suspended solids, are many times those found in domestic wastes and User Charges for most tanneries have or will become a severe financial burden.

The Tanning Industry has been making a concerted effort over the past ten years to develop treatment methods for their wastes. Numerous demonstration grants have been awarded to individual plants both by the Federal Water Quality Administration and the Environmental Protection Agency for the purpose of evaluating the technical and economic feasibility of various treatment methods. The emphasis of the studies carried out to date has primarily been directed toward treatment of effluents as discharged. Only limited efforts have been reported thus far in the U.S. to achieve the desired results through tanning process changes and by reuse and treatment of the wastes in-plant.

Most urban tanneries are unable to apply demonstrated wastewater treatment technologies because of the prohibitive space requirements. The only options available for many plants, therefore, will be to reduce effluent loadings through conservation of water and processing chemicals, by process changes and by pretreatment of selected high strength waste fractions.

Chromium, for example, is a limited as well as a politically-sensitive resource. It is forecast that increasingly difficult prices and availability are forthcoming, making reuse of spent chrome liquors especially important.

The basic objective of this project has been to demonstrate process modifications and wastewater reuse and treatment methods which are technically and economically feasible in effecting major reductions in the total waste load discharged from a large side leather tannery.

The methodology developed through this project, therefore, will be applicable to a large segment of the Tanning Industry. Concomitantly, it should also have a salutary effect on the total waste management effort for those municipalities in which tanneries are located. Additionally, those tanneries which are in a position to employ the more traditional treatment procedures will be provided with alternate methods for achieving the desired and/or required water pollution control objectives.

Measurements have been made and reported in units familiar to and used by the tanning industry. Conversion to the International System of Units (SI) may be made by reference to the "Metric Practice Guide," ASTM E 380-76.

SECTION II

CONCLUSIONS

This work has demonstrated the feasibility of several in-house wastewater management techniques including process changes, recovery and reuse procedures and treatment methods, which mitigate pollution loading.

Hide processors were installed and the traditional hair-save methods of leather production were replaced by a "straight-through" hair-burn process in which soaking, unhairing, bating, pickling and tanning is accomplished within a single processing unit. Besides eliminating numerous hide handling steps, this process change effected a 50% reduction in beamhouse-tanyard effluent volume from an average 107 gallons per side to 54 gallons per side. While much of this water was eventually restored as "sewer-flushes," an overall 38% reduction in 1970 effluent volumes has been observed, primarily due to an intensive water conservation campaign. Consistent with the 50% reduction in lime usage, the pH was lowered from 11.0 to 9.8 with a corresponding 31% reduction in fixed suspended solids. A 71% increase in sulfide loadings was noted due to the required increase in sharpeners for hair pulping. Likewise, total Kjeldahl nitrogen, volatile suspended solids and total volatile solids loadings increased substantially by 79%, 46% and 32%, respectively. Slight increases in Oil and Grease, chloride, BOD-5, COD, total solids, suspended solids and dissolved solids were also recorded. The substantial increase in total chromium loadings from 2.36 to 5.18 lb/1000 lb equivalent green-salted hides is partially due to a designed increase in chrome offered as well as reduced exhaust efficiency in hide processors - dictated ultimately by product quality considerations.

The unit processes and unit operations which could be incorporated into a chrome recovery scheme were investigated and demonstrated using conventional laboratory and pilot-scale procedures. Significant process/equipment design criteria rely heavily on the demonstrations that the choice of alkali for chromium hydroxide precipitation dramatically effects solubility and sludge dewatering characteristics. Hydrated lime was the most effective precipitating agent followed by caustic soda, aqueous ammonia and soda ash. Only lime-precipitated chromium hydroxide reacted favorably with flocculants to form a large, sturdy, settlable floc. An anionic polyelectrolyte, Nalcolyte 677 (Nalco Chemical Company) was optimum at 20-30 ppm.

Dissolved air flotation was ineffective at thickening chromium hydroxide sludges at an air-to-solids ratio of 0.025-to-1.

Gravity settling of lime-precipitated, floculated chromium hydroxide, however, proved highly effective.

The design volumetric loading for chromium hydroxide thickening was established at 400 gpd/ft^2 for the most concentrated chrome-bearing waste fraction generated. The effect of dilution of spent chrome (with wash waters) on design thickener surface area is offset by increased settling rates. Most importantly, within the 2,330 to 6,590 mg/l Cr concentration range, unit areas remain constant at approximately 12 ft^2 per ton of dry solids per day.

Effective dewatering of thickened chromium hydroxide sludge was demonstrated. Hydrated lime and soda ash-precipitated sludges filtered best. Pilot rates of 6.6 and 7.9 gal/ft^2-hr, respectively, with corresponding dry solids rates of 2.1 and 1.6 lb/ft^2-hr were observed.

Production-scale chrome recovery trials demonstrated the recovery of chromium from the most concentrated tanyard wastes generated from eleven (of eighteen) production units daily. Overall, end-of-the-pipe reductions in total chromium are calculated at 37% from an average 5.2 lb to 3.3 lb Cr/1000 lb equivalent green-salted hides. Of the chrome captured, treatment efficiencies in excess of 98% reduction were observed.

Matched sides comparative leather tests revealed no significant difference in leather quality when reacidified chrome was used to replace 23% of the normal production chrome offering. No upper limit for this replacement has yet been determined.

Oxidation of sulfides in unhairing wastes was also investigated in detail to determine the most effective process/system design. Manganese sulfate catalyzed air oxidation was shown to be most economical.

The optimum catalyst dosage fell within the 0.05 to 0.15 Mn^{++}/S$^=$range.

Of the several types of aeration equipment investigated, surprisingly enough, traditional paddle vats were found highly effective, and should be considered a viable alternative when such equipment can be diverted from normal manufacturing uses. The preferred method was identified as surface aeration using floating aerators. Applicable criteria for the specification of such equipment include wastewater volume, sulfide content, catalyst and power costs and available space and time. The sulfide oxidation efficiency of a typical 2 hp floating surface aerator in pilot-scale operations was approximately 1.87 times the manufacturer's oxygen transfer efficiency rating.

On a production-scale, a 10 hp floating surface aerator gave complete oxidation of sulfides in 6,400 gallons of unhairing wastes (including concentrated hair-burn liquors plus half of the wash water from two unhairing runs) from an initial concentration of 2,830 mg/l in 2.75 hours. This is equivalent to a sulfide oxidation aerator efficiency of 5.83 lb S$^=$/hp-hr, or 1.71 times the manufacturer's rated oxygen transfer efficiency. A 98% reduction in sulfide was achieved after only 2.1 hours of aeration. The observed sulfide oxidation aerator efficiency was 2.02 times the rated oxygen transfer efficiency at 6.9 lb S$^=$/hp-hr.

Additional bench-scale investigations identified all tannery waste fractions as highly contaminated with Oil and Grease. Segregated spent chrome and pickle liquors may be treated by simple gravity flotation (1 hour retention) to effect 95 and 89% reductions, respectively. On a production-scale, a 10,000 gallon "batch" of spent chrome liquor was treated by gravity flotation for a 92% separation. An additional 7% of the Oil and Grease was recycled with the recovered chrome while only slighly more than 1% was actually sewered. Flotation for "removal" of Oil and Grease was ineffective for soaking, unhairing, relime, and bating liquors.

Detailed sampling and analyses of individual beamhouse and tanyard waste fractions revealed unhairing wastes as the most highly contaminated. This waste fraction (excluding relime) contributes 19%, 33%, and 30% to the total effluent BOD, COD and suspended solids loadings, respectively. Crude protein can be precipitated from unhairing waste to effect a major reduction in these contaminants. In bench-scale experiments, oxidized hair-burn liquor was acidified to generate a rapidly settling protein precipitate. After 60 minutes settling, COD reductions up to 79% were observed. The optimum pH for precipitation was within the 0.9 to 5.0 range, while the minimum sludge volume obtained was within the 1.0 to 3.9 pH range.

SECTION III

RECOMMENDATIONS

Several of the process/equipment specification and design criteria developed during this project have been adopted in production-scale chrome recovery and sulfide oxidation systems. Further work must be undertaken to optimize these installations. In particular, the effect of around-the-clock operation of the chrome recovery system must be studied to determine "continuous" chromium and Oil and Grease removal efficiencies. Likewise, operation of the sulfide oxidation system must be coordinated with typical production scheduling to demonstrate optimum sulfide reductions.

The reductions in overall tannery chromium and sulfide loadings due to these wastewater management techniques have been calculated. However, further sampling and analyses will be required to characterize the more subtile interactions among these "changed" waste-streams which are currently only hypothesized.

Because of the demonstrated wide differences in the effects of various alkalis on chrome recovery efficiencies, additional alkali studies including calcium carbonate, sodium carbonate, magnesium oxide and magnesium carbonate must be investigated along with alternative coagulants and flocculants.

Flotation by in situ generation of CO_2 should be pursued further as a possible alternative to present chromium hydroxide thickening techniques.

Additional work is also warranted to determine the effectiveness of flotation for treating segregated tannery waste fractions, as well as combined tannery effluents.

The aeration requirement for the batch oxidation of sulfides in unhairing wastes has been determined using a catalyst dosage within the apparent optimum range. Additional work is required to define the catalyst dosage - aeration interactions outside of this catalyst range. These interactions will determine the optimum design for sulfide oxidation.

The hydrocyclonic separation of calcium sulfate from reacidified chrome is a major process innovation in the chrome recovery system. However, in light of the unspectacular removal efficiencies observed, various operating parameters including flow, pressure and orifice diameter should be studied to "optimize" this separation. Also, this unit operation should be investigated as a tool for the treatment of suspended solids in other waste fractions.

SECTION IV

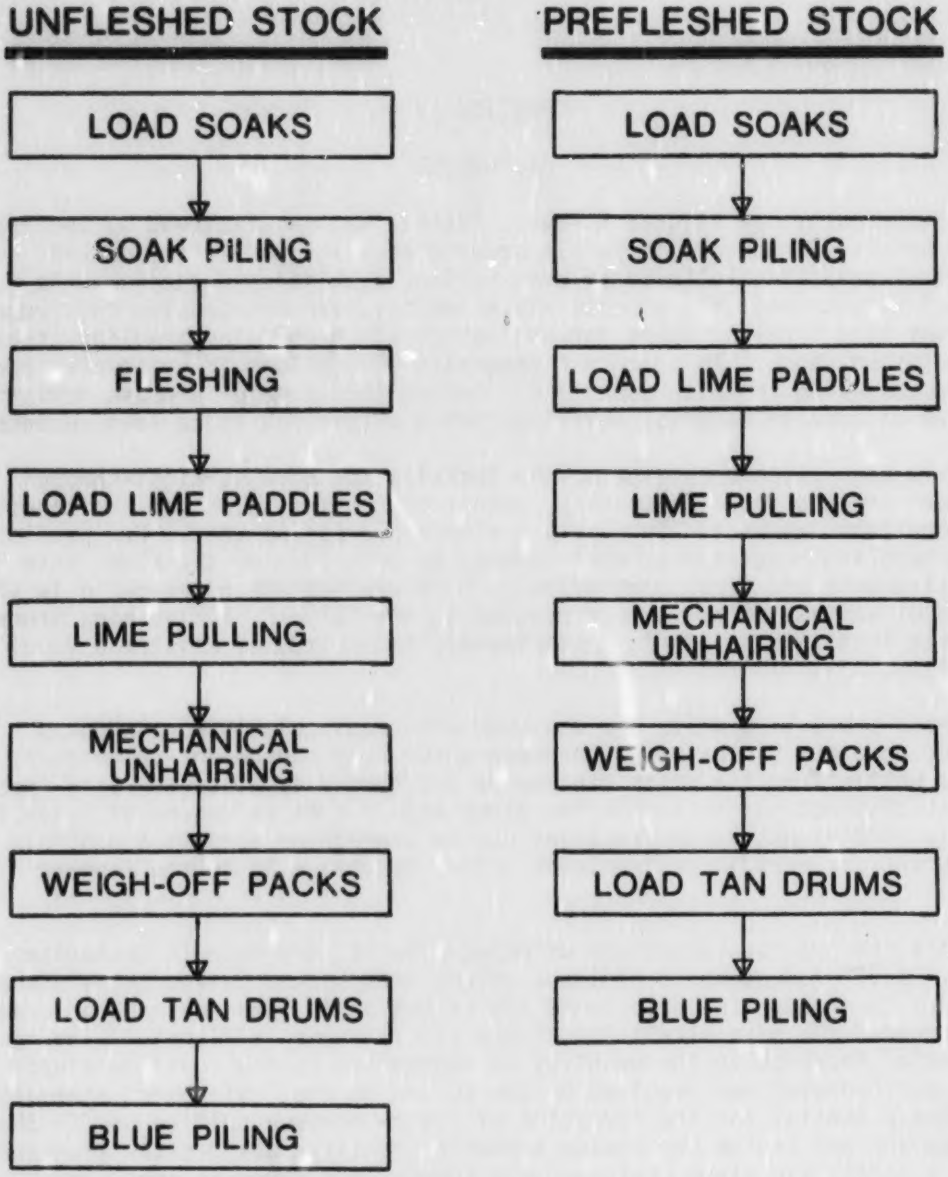
BACKGROUND

Historically, at Pfister & Vogel, leather was manufactured by the traditional hair-save method with paddle or drum soaking, paddle liming and mechanical unhairing followed by drum bating, pickling and tanning. As Figure 1 illustrates, the process was a lengthy, labor-intensive one, requiring eight hide handling steps for prefleshed stock and nine handling steps for unfleshed stock. This process generated 107 gallons of wastewater per side processed to the blue condition. During 1972 a major process revision was made to improve material handling, process time and space requirements.

This conversion consisted of the installation of a straight-through, hair-burn process in which soaking, unhairing, bating, pickling and tanning is accomplished sequentially within a single processing unit. For prefleshed hides, handling requirements were reduced to only loading the hides into the processing unit and final blue piling. This new process generated only 54 gallons of wastewater per side processed to the "blue." Twelve hide processors were installed to handle approximately two-thirds of Pfister & Vogel's production.

These processing units are equipped with recirculating/drain pumps introducing a new dimension to in-house wastewater management techniques. Process wastes from the units can now be discharged as discrete waste fractions at distinct points within the plant with a greater degree of hydraulic control. Individual waste fractions can be segregated through a manifold arrangement for recycle or treatment before discharge to common tannery sewers.

This new process technology effected a marked decrease in wastewater volume. A 50% reduction in effluent volume from beamhouse and tanyard operations was observed. The programmed 50% reduction in lime consumption drastically reduced the mean alkalinity of the total tannery effluent. Also, a substantial increase in the quantity of sharpeners (sodium sulfide and/or sodium sulfhydrate) was required by the switch to the "hair-burn" approach. Thus, the potential for the formation of toxic hydrogen sulfide gas in the plant sewers and inside the sewage screening facility was greatly increased. Numerous safety and alarm measures were adopted and sewer flushes were installed to augment sewer flows, provide needed dilution, reduce retention times and reduce this hazard. The increased flow to meet these safety and housekeeping measures unfortunately offset most of the designed reduction in process effluent volume.


UNFLESHED STOCK
LOAD SOAKS
SOAK PILING
FLESHING
LOAD LIME PADDLES
LIME PULLING
MECHANICAL UNHAIRING
WEIGH-OFF PACKS
LOAD TAN DRUMS
BLUE PILING
PREFLESHED STOCK
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SOAK PILING
LOAD LIME PADDLES
LIME PULLING
MECHANICAL UNHAIRING
WEIGH-OFF PACKS
LOAD TAN DRUMS
BLUE PILING

Figure 1: HIDE HANDLING STEPS FOR TRADITIONAL HAIR-SAVE PROCESS.

SECTION V

WASTE SURVEYS

The effect of Pfister & Vogel's conversion from a paddle soak - paddle lime - drum bate, pickle, tan-hair-save process to a "straight-through" hair-burn process on effluent loadings is shown in Table 1. It should be noted that numerous process modifications made concomitant with the change-over were dictated by the need for adjustments in leather properties. These modifications contributed significantly to the ultimate hair-burn process waste profile. A 38% reduction in 1970 effluent volumes was observed from 8,960 gallons per 1000 lbs of equivalent green-salted hides charged to the process to the current level of 5,550 gallons per 1000 lbs of hides. Only a portion of this reduction, however, is attributable to the process conversion. While beamhouse/tanyard process waste volumes were reduced 50% from 3,970 gallons per 1000 lbs in 1970 to the current 1,980 gallons per 1000 lbs, an additional 1,330 gallons of water per 1000 lbs had to be put back into the system as a safety and housekeeping requirement to insure adequate flushing of internal sewers.

TABLE 1. EFFECT OF PROCESS CHANGE ON WASTEWATER LOADINGS

	Loading, lb/1000 lb green-salted hides*	
Parameter	Hair-Save	Hair-Burn
Flow	8,960	5,550
pH	10.8-11.2	8.9-10.7
BOD - 5 (20^{o}C)	62.4	66.9
COD	185	211
Oil & Grease	22.0	28.4
Chloride as Cl^-	106	119
Alkalinity as $CaCO_3$	-	56.8
Calcium as Ca^{++}	23.6	-
Sulfide as $S^=$	1.87	3.20
Kjeldahl N as N	8.77	15.7
Ammonia N as N	3.29	4.64
Total Solids	451	486
Suspended Solids	136	149
Dissolved Solids	315	337
Total Fixed Solids	338	340
Total Volatile Solids	113	146
Fixed Suspended Solids	64	44
Volatile Suspended Solids	72	105
Chromium as Cr	2.36	5.18

* Except for flow in gallons/1000 lb and pH which is unitless.

Most of the observed flow reduction was due to an intensive water conservation program. A major element of this program was the incorporation of a gravity screening and water recirculation system for the wet collection of buffing dust. This recycle alone effected a wastewater reduction of nearly one quarter million gallons per day while reducing wastewater effluent loadings by an estimated 200 lbs of suspended solids per day in the form of screened and separated, wet buffing dust.

The data presented in Table 1 are calculated loadings of various wastewater parameters per 1000 lbs of equivalent green-salted hides. The actual Pfister & Vogel rawstock mix consists of varying proportions of green-salted cattle hides and prefleshed, brine cured cattle hides dependent upon relative quality, price, availability and finished leather requirements. The observed raw stock mix ranged from 22% to 100% prefleshed hides on the sampling days and all loadings have been adjusted to an equivalent green-salted hide weight basis to provide a common denominator. The equivalent green-salted weight was extrapolated from Pfister & Vogel's production experience which indicates that each pound of prefleshed brine cured hide is equivalent to 1.28 lbs of conventional, green-salted hides. Effluent samples were composited (in proportion to flow) from 15-minute-incremental grab samples taken immediately downstream from the 5/32" rotary wastewater screen, over a twenty-four hour period - and were analyzed according to Standard Methods. Flow was measured by a "pump-on-time" totalizer connected in parallel with flow-calibrated industrial sewage pumps. These data confirm the expected reduction in pH and fixed suspended solids consistent with a 50% reduction in lime usage. Likewise, the marked increase in sulfide from 1.87 to 3.20 lb/1000 lb is due to the required increase in sharpeners for hair pulping. The total solids increased only slightly while there was a considerable change in the proportions of fixed and volatile residues. Most notably, total volatile solids and volatile suspended solids increased 32% and 46%, respectively, while total Kjeldahl nitrogen was boosted by 79% to 15.7 lb/1000 lb. This process conversion more than offset any reduction due to buffing dust screening with net increases in BOD-5 and total suspended solids of 7% and 14%, respectively. A slight increase in the COD-to-BOD ratio from 2.96:1 to 3.15:1 was observed.

The effluent loading due to each "lower tannery" subprocess wastewater discharge was determined for a typical hide processor run in which prefleshed, brine cured hides were used as rawstock. Twenty-four discrete process discharges were sampled covering the most concentrated process floats through the most diluted wash waters. After determination of the volume and strength of each waste fraction, the appropriate loadings were grouped and the total pollution profile attributable to the unit processes of soaking, liming, bating, pickling and tanning were calculated. These data are compiled in Table 2.

TABLE 2. WASTEWATER LOADINGS FOR LEATHER MANUFACTURING SUBPROCESSES

Subprocess wastewater loadings in lb/1000 lb equiv. green-salted hides*	Soak	Lime	Relime	Bate	Pickle	Tan	Sub-Total	Post-tan	24 hr Composite
pH	9.8- 10.1	11.6- 12.2	12.3- 13.1	8.9- 9.1	2.7	2.9- 3.4			
BOD(20°C)	9.9	15	5.6	5.0	1.1	3.8	40	6.5	67
COD	13	75	13	6.3	3.6	13	120	56	210
Oil & Grease	6.0	4.0	1.6	2.0	0.42	5.2	19	4.7	28
Chloride as Cl^-	33	45	9.4	2.9	7.6	15	110	4.4	120
Alkalinity as $CaCO_3$	7.8	31	33	3.9	-	-	76	-	57
Acidity as $CaCO_3$	-	-	-	-	1.1	10	11	-	-
Sulfide as $S^=$	-	4.8	1.2	0.067	0.005	0	6.1	-	3.2
Kjeldahl N as N	0.54	5.1	1.3	5.9	0.25	0.89	14	0.88	16
Ammonia N as N	-	-	-	4.6	-	-	4.6	0.19	4.6
Total Solids	88	120	41	44	20	92	400	59	490
Susp. Solids	12	34	13	8.8	0.66	2.6	70	14	150
Dis. Solids	77	83	28	35	19	89	330	44	340
Tot. Fixed Sol.	69	86	35	20	16	75	300	23	340
Tot. Vol. Sol.	19	31	5.8	24	4.0	17	100	34	150
Fixed Susp. Sol.	5.0	17	11	4.5	0.27	0.47	38	0.38	44
Vol. Susp. Sol.	6.6	17	2.2	4.2	0.38	2.2	32	14	100
Chromium as Cr	-	-	-	-	-	4.3	4.3	1.6	5.2

* except pH which is unitless

The COD/BOD ratios for the various lower tannery process wastewaters ranged from 1.28:1 for bating wastes to 4.99:1 for unhairing. Also, a ratio of 8.61:1 for post-tan operations including blue stock wringing, coloring, retan, fatliquoring and finishing was observed. This exceptionally high COD/BOD ratio is probably due to the presence of spent vegetable tannins from retan operations.

All of the processing steps contribute significant quantities of BOD, COD, Oil & Grease, chloride, nitrogen and residues to total effluent loadings. Unhairing wastes are the most highly concentrated, however, and contain most of the sulfide together with an appreciable amount of alkalinity.

The contaminants are so widely distributed throughout all of these process waste fractions that no segment may be overlooked as insignificant. For example, the pollutants generated per thousand pounds of equivalent green-salted hides from soaking, unhairing and reliming each individually exceeds the EPA's Best Practicable Effluent Limitations for subcategory one tanneries (c.f. 40 CFR Chapter 1, Subchapter N: Part 425 Subpart A, 39 FR 12960, Apr. 9, 1974) [since remanded] for pH, BOD, TSS and Oil & Grease. Bating process wastes exceed BPCT limits for BOD, Oil & Grease, and TSS: pickling wastes exceed the pH limitations; and tanning wastes exceed the limits for pH, Oil & Grease and total chromium. Every processing step, except pickling, exceeds the "Best Available Technology Economically Achievable" (1983) limits for total Kjeldahl nitrogen, while only the soaking and tanning fractions do not exceed the 1983 limitations on sulfide.

Finally, the characteristics of the combined wastewater generated from all tannery operations after blue piling (including blue stock wringing but excluding beamhouse and tanyard wastes) are also depicted in Table 2. These wastes which contribute roughly 40% to the total tannery effluent volume independently exceed 1977 limits for BOD, TSS, total chromium and Oil & Grease and also exceed the 1983 limit for total Kjeldahl nitrogen. It is obvious that while certain process waste fractions have been identified as more highly contaminated than others, no one process discharge can be singled out for treatment, recovery or reuse under the expectation of "eliminating" a specific, major wastewater contaminant from the final effluent. As the unhairing wastes and chrome tanning wastes are among the most highly contaminated, treatment of these fractions has received first priority. Sulfide oxidation and chrome recovery are discussed later.

The Oil & Grease component of our total tannery effluent was further characterized. Aliquots of a typical 24-hour effluent sample taken downstream from our rotary screen and composited in proportion to flow were treated according to the procedure for Grease outlined in Standard Methods ed. 13., Part 209A. The residues obtained were further analyzed by infrared spectroscopy and computerized gas chromatography/mass spectrometry. No hydrocarbons of the type expected from petroleum products were present. The extracted "Greases" were identified as animal fats and/or vegetable oils.

SECTION VI

CHROME RECOVERY FEASIBILITY STUDIES

A review of the literature shows that while the recovery and reuse of chrome tanning agents is indeed feasible, there is little laboratory or pilot data available which can be used for designing chrome recovery systems.

The purpose of this study was to develop, through laboratory and pilot-scale investigations, pertinent design data for the unit processes and unit operations employed in the recovery of chromium from spent chrome tanning liquors.

LITERATURE REVIEW

The recovery and reuse of chromium tanning agents has been reported by many investigators. Harnly (2) reported the successful recycle of chrome during World War II by precipitation with caustic soda followed by decantation, acidification and restrengthening. Benrud (3) reported seven serial reuses of chrome liquors by refortification. Miller (4) reported the reuse of chrome over a period of six weeks through replenishment with dry chromium salt, sulfuric acid and sodium chloride with no significant build-up of sulfates. Davis and Scroggie (5) also demonstrated on a pilot scale that several commercially prepared chrome tans could be reused at least 13 times by float adjustment and restrengthening. They reported that the recycle, resulting in a 25% reduction in chrome usage, did not adversely affect either the subjective or physical properties of the resultant leather.

Additional work by Davis and Scroggie (6) showed that the species of chromium complexes present in tanning liquors, throughout the range of molecular weights and charge distributions as measured by gel filtration chromatography, were taken up by hide. Exhaust liquors from these commercial chrome tannages were found to exhibit the same distribution of chromium species as the original chrome liquors.

According to Petruschke (7) the most promising alternative to reuse through replenishment is precipitation with alkali followed by filtration, washing and redissolving of the recovered chromium hydroxide. Hauck (8) reported that calcium hydroxide, sodium hydroxide, ammonium hydroxide, sodium bicarbonate and soda ash had been used to precipitate chromium hydroxide from spent chrome; and that the selection of alkali should depend on a number of factors including the optimum pH for precipitation. He also suggested that a rotary vacuum drum filter might be effective in dewatering chromium hydroxide sludges.

Young (9) demonstrated that chromium hydroxide slurry could be concentrated by pressure filtration. To optimize this pressure filtration, it was suggested that the sludge be thickened by settling prior to filtration, with a flocculating agent added to enhance settling rates. An anionic polymer appeared to give the best results.

Weber (10) calculated that recovery of chrome by ion exchange would be prohibitively expensive because of the blockage of exchange columns and high regeneration costs.

For precipitating chromium hydroxide from spent chrome liquors, Weber concluded that lime was the "best" alkali. He also noted that "mechanical dehydration" was effective in dewatering chromium hydroxide sludges.

Das et al. (11) used sodium carbonate for precipitating chromium hydroxide. The precipitate was filtered and the filter cake dissolved in hot sulfuric acid. The basicity of the reacidified chrome was then adjusted for subsequent reuse. Abramovich (12) reported that "fresh" calcium hydroxide was more effective in precipitating chromium hydroxide than were alkaline beamhouse effluents. Sodium hydroxide and ammonium hydroxide were used by Bianchi (13) to precipitate chromium salts from spent chrome solutions. After filtration, the precipitate was washed and boiled in dilute sodium hydroxide followed by dilution and a second filtration. The recovered chromium was dissolved in sulfuric acid and used in the preparation of new tanning baths.

The literature review leads the authors to conclude that the current practice of chromium recovery from spent chrome tanning liquors would benefit immensely by a systematic evaluation of the design parameters applicable to chrome recovery systems.

It has been demonstrated, for example, that several alkalis can be used successfully to precipitate chromium hydroxide from spent chrome tanning liquor, however, little is known about the effect of alkali type on the unit processes and unit operations employed. Likewise, little is known about the effect of alkali type on the flocculation and settling of chromium hydroxide.

It is suggested in the literature review that vacuum filtration might be used to dewater precipitated chromium hydroxide, however, filtration rates, which are essential for sizing such equipment have not been reported.

Thus, the major objective of this phase of the project was to investigate the unit processes and unit operations which could be incorporated in a chrome recovery scheme; and to establish through conventional laboratory and pilot-scale procedures representative data for the design of a chrome recovery system.

Typical values of significant waste parameters for the spent chrome liquor employed in this study are presented in Table 3. These values represent the concentrated spent chrome waste fractions and do not include subsequent wash waters.

In practice, washes are commonly used after tanning to remove insoluble matter such as bits of flesh and fats and greases, as well as soluble salts from the surface of the tanned hides. The wash water volume may be as much as five times that of the original float volume. The design of any chromium treatment or recovery process must take into account this variation in chrome concentration of the wastes generated, i.e., concentrated liquors followed by large volumes of dilute wash waters.

TABLE 3. TYPICAL ANALYSIS OF CONCENTRATED SPENT CHROME

Parameter	Concentration, mg/l*
Chromium (as Cr)	6,260
Acidity (as $CaCO_3$)	15,000
pH	3.30
Oil & Grease	6,310
Chlorides (as Cl^-)	18,200
BOD-5 (20°C)	4,920
COD	18,900
Total Solids	116,200
Total Fixed Solids	92,220
Total Suspended Solids	3,760
Fixed Suspended Solids	840
Total Kjeldahl N (as N)	1,110

* Except pH which is unitless.

PRECIPITATION OF CHROMIUM HYDROXIDE

Chromium is a transition element, and in its 3+ oxidation state shows a strong tendency to complex with a wide variety of ligands to form coordination compounds - most of them highly colored. Among the simplest of the Cr^{3+} complexes is $Cr(H_2O)_6^{3+}$ or hexaquochromium (III). This violet colored complex is a weak acid which readily undergoes hydrolysis. Hydrolysis proceeds as the acidity of a solution of $Cr(H_2O)_6^{3+}$ is decreased until above pH 5, the grey-green, hydrated Cr^{3+} hydroxide precipitates.

$$[Cr(H_2O)_6]^{3+} + H_2O = [CrOH(H_2O)_5]^{++} + H_3O^+$$

$$[CrOH(H_2O)_5]^{++} + H_2O = [Cr(OH)_2(H_2O)_4]^+ H_3O^+$$

$$[Cr(OH)_2(H_2O)_4]^+ + H_2O = [Cr(OH)_3(H_2O)_3](s) + H_3O^+$$

Commonly the third hydrolysis product is denoted as $Cr(OH)_3$ (chromium hydroxide) or Cr_2O_3 (chromic oxide).

The precipitation of hydrated Cr^{3+} as the hydroxide is usually expressed by the simpler notation:

$$Cr^{3+} + 3OH^- = Cr(OH)_3(s)$$

The solubility product, K_{sp}, for chromium hydroxide is reported by Hognes et al. (14) to be:

$$K_{sp} = \left[Cr^{3+}\right] \times \left[OH^{-}\right]_3 = 7 \times 10^{-31}$$

The degree of hydrolysis of $\left[Cr(H_2O)_6\right]^{3+}$ is termed basicity. Basicity is a ratio calculated from analytical values for the chromium concentration and the titratable acidity. According to the American Leather Chemists Association Method C10, basicity is calculated from the following formula:

$$\text{Basicity (percent)} = \frac{A - B}{A} \times 100$$

where

A = milliequivalents (me) of Cr_2O_3 per liter (ALCA Method C1)

B = titratable acidity in milliequivalents per liter (ALCA Method C5)

Thus, theoretically, the acidic species $[Cr(H_2O)_6]^{3+}$ has a basicity of 0% and the precipitated $Cr(OH)_3(H_2O)_3$ has a basicity of 100%. Between these extremes, any degree of basicity is attainable.

In "pure" solutions, the concentration of Cr^{3+} is a function of the hydroxyl ion concentration and therefore pH. At acidic and neutral pHs the solubility of Cr^{3+} is attributable to a common ion effect. Trivalent chromium, however, is amphoteric so that $Cr(OH)_3$ dissolves in the presence of excess hydroxyl ion to form anionic chromium complexes.

The optimum pH for the precipitation of chromium hydroxide from spent chrome tanning liquor was demonstrated by varying dosages of sodium hydroxide added to a concentrated spent chrome solution.

The standard jar test procedure was followed using a six-place variable speed mixing apparatus and six 1000 ml Pyrex beakers. To each of the six beakers 500 ml of spent chrome at a concentration of 5800 mg/l Cr was added. The acidity of this solution was 300 me/l. A theoretical dosage of 150 me of sodium hydroxide was required to precipitate the chromium hydroxide stoichiometrically. Therefore, the dosages of 2N sodium hydroxide added for neutralization were varied from 110 me to 190 me corresponding to a range of 83%-125% of the titratable acidity as determined by the ALCA Method C5. After the alkali addition, the six samples were diluted to final volumes of 600 ml. The samples were mixed at 100 rpm for two minutes followed by an additional 20 minutes of slow mixing at 30 rpm and then were allowed to settle under quiescent conditions.

There was no noticeable settling within the first four hours. After 24 hours, however, the precipitated chromium hydroxide had settled enough to withdraw a sample of supernatant for analysis. The effect of alkali dosage on pH, chromium concentration of the supernatant and on sludge volume is illustrated in Table 4.

The pH values from 8.55 to 9.70 lie within the expected optimum range for the precipitation of chromium hydroxide. Notably, the corresponding alkali dosages ranging from 91% to 117% of the stoichiometric requirement for 100% basicity yielded supernatant chromium concentrations which did not differ significantly.

To determine the relative effectiveness of different alkalis to precipitate chromium hydroxide from spent tanning liquors the same procedure used for caustic soda was repeated using hydrated lime, aqueous ammonia and soda ash, respectively. The comparative effectiveness of these alkalis is illustrated in Figure 2.

The calculated amounts of calcium hydroxide were suspended in 100 ml of distilled water and added to each of six 500 ml spent chrome samples followed by five minutes of rapid mixing at 100 rpm and 20 minutes of slow mixing at 30 rpm. Alkali dosages were varied from 85% to 140% of the stoichiometric equivalent required for 100% basicity. To one sample, after the addition of lime and mixing, 80 mg/l of an anionic liquid polymer, Nalcolyte 677, was added as a 0.1% solution followed by a five minute rapid mix and 20 minutes of slow mixing.

TABLE 4. EFFECT OF NaOH DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE

NaOH Dosage,me/l	% NaOH	pH	Supernatant Cr,mg/l	Sludge,ml
250	83	8.25	4.74	420
275	91	8.55	2.44	430
300	100	8.85	2.74	450
325	108	9.38	2.50	440
350	117	9.70	2.38	435
375	125	10.10	5.[illegible]5	420

The spent chrome samples used in the lime-precipitation study initially contained 6690 mg/l of chromium (385.5 me/l) and had an acidity of 343 me/l. A $Ca(OH)_2$ dosage of 343 me/l, therefore, was required to increase the basicity to 100%.

The effect of hydrated lime on the precipitation of chromium hydroxide is summarized in Table 5.

Chromium hydroxide sludge settled faster with hydrated lime when other precipitating agents were used. The sludge volume was smaller and the concentration of chromium in the supernatant liquid was lower. The lowest supernatant chromium concentration obtained after 24 hours of quiescent settling was 0.10 mg/l when 140% alkali was used. The supernatant chromium concentration at 100% alkali was 0.90 mg/l. The improved separation at the higher alkali level was achieved, however, at the cost of increasing the sludge volume by nearly 10%.

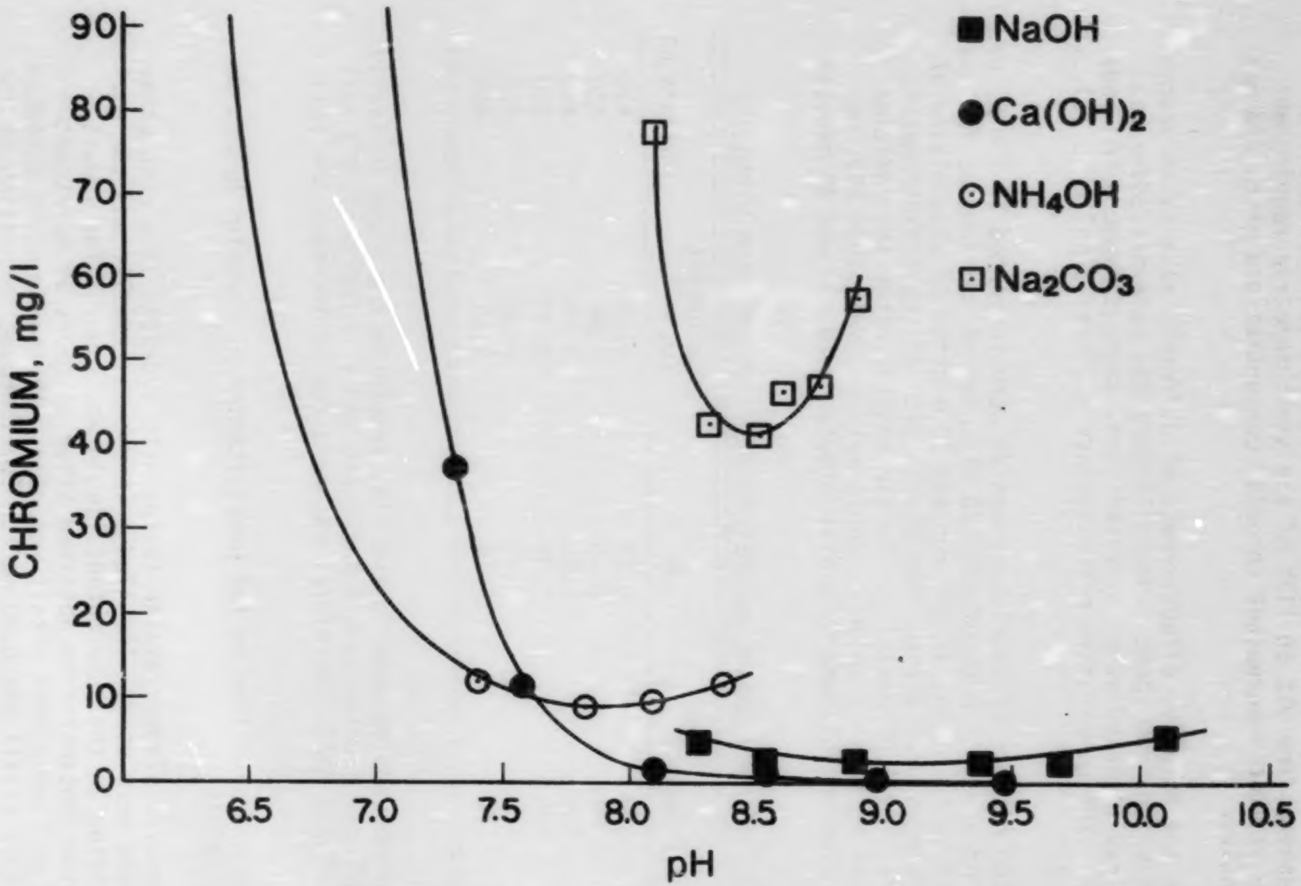

Figure 2: EFFECT OF pH ON SUPERNATANT CHROMIUM CONCENTRATIONS.

The polymer addition dramatically improved the settling of the suspended chromium hydroxide such that a final effluent concentration of 0.16 mg/l Cr after 24 hours could be expected with 100% alkali addition.

TABLE 5. EFFECT OF $Ca(OH)_2$ DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE - PART I

$Ca(OH)_2$ Dosage,me/l	% Alkali	pH	Supernatant Cr,mg/l	Sludge,ml
209	60	6.45	1,100	250
274	80	7.68	414	300
343	100	8.55	0.96	345
404	120	8.98	0.50	375
470	140	9.48	0.10	375
343*	100	8.45	0.16	350

* 100% alkali dosage plus 80 mg/l of Nalcolyte 677

From Figure 2, it is apparent that the pH range employed in lime-precipitation did not demonstrate the increased solubility of chromium at higher pH values predicted from the amphoteric nature of these chrome salts. Therefore, a second series of lime-precipitation runs was conducted using $Ca(OH)_2$ dosages ranging from 85% to 350% of the stoichiometric requirement for precipitation. The spent chrome employed in these latter runs which also contained 6,690 mg/l of chromium but an acidity of 265 me/l was screened (0.040" openings) and skimmed to effect an approximate 90% reduction in Oil & Grease. As shown in Table 6, after 24 hours of quiescent settling, supernatant chromium levels ranged from 37.8 mg/l at pH 7.3 to 0.10 mg/l at pH 11.9. The chromium solubility increased to 0.24 mg/l at pH 12.7. The optimum pH for lime-precipitation was shown to lie within the 8.7 to 12.7 range.

When aqueous ammonia was used as the precipitating agent in the range of 73% to 125% of the stoichiometric requirement, the optimum precipitation of the $Cr(OH)_3$ occurred at a pH of 7.82. The chromium concentration in the supernatant liquid after 24 hours of quiescent settling was 8.84 mg/l.

TABLE 6. EFFECT OF $Ca(OH)_2$ DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE - PART II

$Ca(OH)_2$ Dosage,me/l	% Alkali	pH	Supernatant Cr,mg/l	Sludge,ml
224	85	7.30	37.8	320
264	100	7.58	11.3	300
330	125	8.11	1.30	320
396	150	8.70	0.59	400
660	250	11.90	0.10	430
924	350	12.70	0.24	430

The difference observed in the optimum pH for caustic soda and ammonium hydroxide probably results from the formation of soluble chromium-ammonia complexes at the higher pH values.

The spent chrome samples contained 5,800 mg/l of chromium and had an acidity of 300 me/l. The alkali dosage therefore required to raise the basicity to 100% was 300 me/l. The results of the ammonium hydroxide precipitation of chromium hydroxide from spent chrome tanning liquor are shown in Table 7.

TABLE 7. EFFECT OF NH_4OH DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE

NH_4OH Dosage,me/l	% Alkali	pH	Supernatant Cr,mg/l	Sludge,ml
220	73	6.38	137	410
260	87	7.40	11.5	420
300	100	7.82	8.84	435
340	113	8.10	9.98	440
380	126	8.28	11.9	440

Sodium carbonate was demonstrated to be the least effective precipitating agent. The spent chrome used for precipitation by soda ash contained 6,180 mg/l of chromium and had an acidity of 298 me/l. Dosages of Na_2CO_3 were varied from 75% to 137% of the alkali requirement. As shown in Table 8, the optimum dosage was between 87% and 100% alkali, corresponding to supernatant pH's of 8.30-8.48. The supernatant chromium concentration within this dosage range varied from 40.5 mg/l to 41.5 mg/l.

TABLE 8. EFFECT OF Na_2CO_3 DOSAGE ON PRECIPITATION OF CHROMIUM HYDROXIDE

NA_2CO_3 Dosage,me/l	% Alkali	pH	Supernatant Cr,mg/l	Sludge,ml
224	75	8.12	77.5	400
260	87	8.30	41.5	410
298	100	8.48	40.5	440
335	112	8.60	45.6	450
372	125	8.75	46.2	450
410	137	8.91	56.8	445

Several important conclusions can be drawn regarding the precipitation of chromium hydroxide from spent chrome tanning liquors. These studies demonstrated that solubility is highly dependent on pH, and that the optimum pH varies depending on the alkali used. Interestingly, also we found that the optimum dosage for each of the alkalis used was 100% of the acidity as measured by the ALCA Method C5.

An additional finding was that the type of alkali used to precipitate the chromium hydroxide has a significant effect on the concentration of Cr^{3+} found in the supernatant liquor. The order of effectiveness for removal of chromium hydroxide was determined to be calcium hydroxide> sodium hydroxide> ammonium hydroxide> sodium carbonate.

Finally, Nalcolyte 677 proved to be an effective flocculating agent especially when hydrated lime was used for precipitation. This polymer effected immediate flocculation and substantially faster settling as well as improved supernatant clarity and lower supernatant chromium concentrations after 24 hours. The polymer only slightly improved settling characteristics when alkalis other than lime were used. The effectiveness of lime as a coagulant is probably related to its ability to provide a nucleus of high charge-to-area ratio within the pH range employed. Also, a denser floc is probably formed because of the co-precipitation of insoluble calcium sulfate.

COAGULATION AND FLOCCULATION OF CHROMIUM HYDROXIDE

Under optimum conditions for the precipitation of chromium hydroxide from spent chrome liquors, an extremely fine, slow settling, amorphous, blue-green precipitate is formed. Factors contributing to the slow rate of settling probably include repulsive, electrostatic forces at the surface of the chromium hydroxide particle, and the high affinity of $Cr(OH)_3$ for water. Thus, aggregation into dense, settleable particles is inhibited.

Since the chemistry of Al^{3+} is in many ways similar to that of Cr^{3+} and since small amounts of aluminum would not interfere with anticipated reuses of the chrome, it was hypothesized that aluminum sulfate was the best coagulant that might be used to "destabilize" the chromium hydroxide suspension. Further, trivalent aluminum, in accordance with the Schultz-Hardy Rule (15) was expected to be a far more effective coagulant than a mono or divalent ion.

Studies using a coagulant to improve suspended solids removal were conducted. Six 500 ml samples containing 5,800 mg/l of chromium were neutralized with 2N NaOH to pH 9.0. The samples were mixed at 100 rpm for five minutes then 20 minutes at 30 rpm. Varying amounts of a fresh solution of $Al_2(SO_4)_3 \cdot 18\ H_2O$ containing 5,000 mg/l of Al^{3+} were added and the pH was re-adjusted to 9.0 with sodium hydroxide. After adjusting the volume to 600 ml, the samples were rapidly mixed for 5 minutes, slow-mixed for another 20 minutes and then allowed to settle. Al^{3+} concentrations up to 500 mg/l gave no significant change in the rate of settling of the precipitated chromium hydroxide.

Further attempts to agglomerate the chromium hydroxide were made using two anionic polyelectrolytes (Nalcolyte 677 and Rohm and Haas A-10) and a cationic polymer (Buckman Bubond 60). Addition of 80 mg/l of Nalcolyte 677 to sodium hydroxide-precipitated chromium hydroxide at pH 9.0, definitely improved the rate of settling, whereas the other polymers did not produce a noticeable change in the settling rate. The effect of the addition of Nalcolyte 677 is illustrated in Figure 3. Slightly improved floc formation resulted in significantly improved settling.

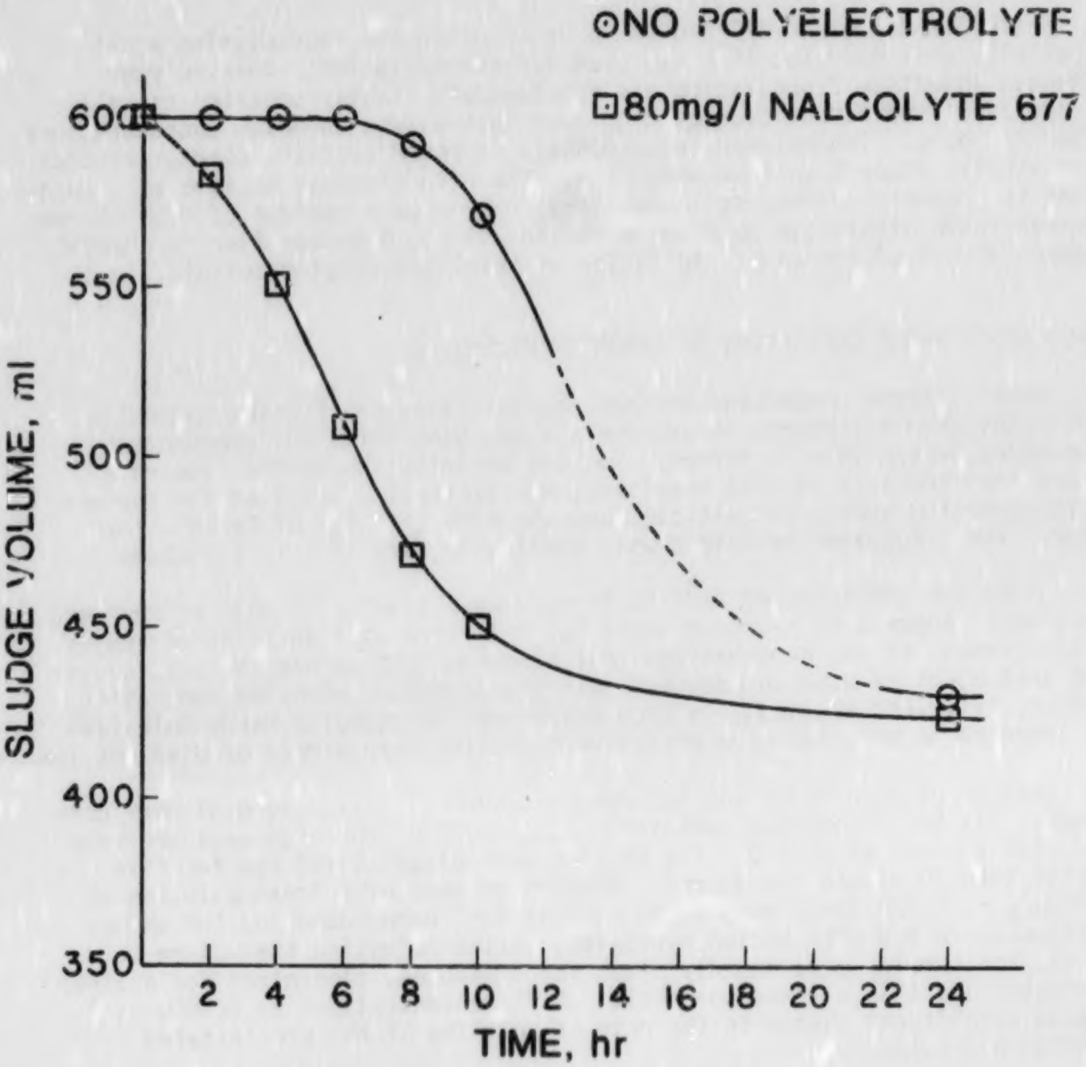

Figure 3: EFFECT OF NALCOLYTE 677 ON THE SETTLING OF NaOH-PRECIPITATED CHROMIUM HYDROXIDE.

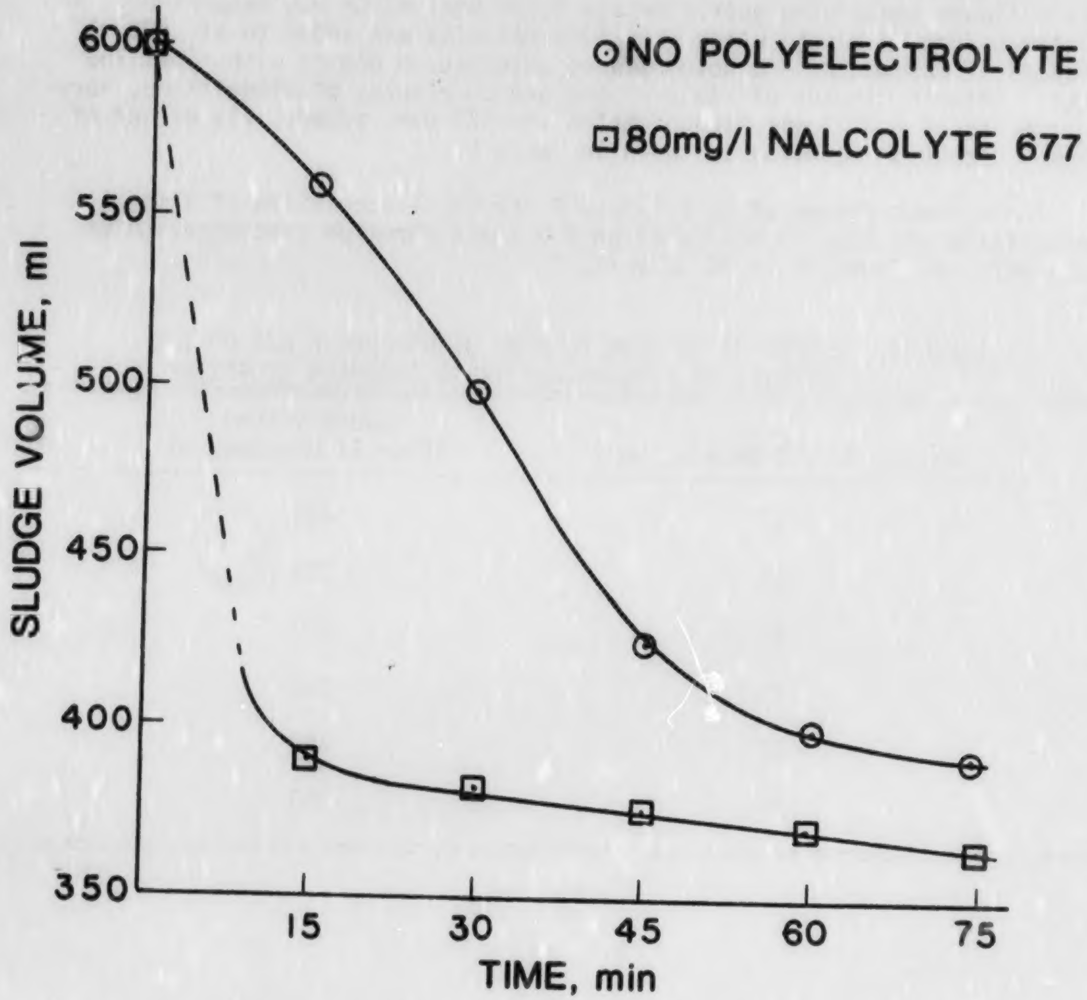

Figure 4: EFFECT OF NALCOLYTE 677 ON THE SETTLING OF $Ca(OH)_2$-PRECIPITATED CHROMIUM HYDROXIDE.

The addition of polyelectrolytes to the ammonium hydroxide, or soda ash-precipitated chromium hydroxide did not improve the settleability of these sludges. By contrast, the addition of 80 mg/l of polyelectrolyte to lime-precipitated chrome resulted in the immediate formation of a large, sturdy, rapidly settling floc. The effect of Nalcolyte 677 on the settling of lime-precipitated chromium hydroxide is shown in Figure 4.

The optimum dosage of Nalcolyte 677 for the coagulation of a spent chrome liquor containing approximately 5,000 mg/l of Cr was determined. A calcium hydroxide dosage which gave 100% basicity was added to six 500 ml aliquots of chrome and the volumes were adjusted to 600 ml with distilled water. After 5 minutes of rapid-mixing and 20 minutes of slow-mixing, varying amounts of a 0.5% solution of Nalcolyte 677 were added. The effect of polymer dosage on settling is shown in Table 9.

The optimum dosage of Nalcolyte 677 for the flocculation of lime-precipitated chromium hydroxide at pH 9.0 and a chromium concentration of 4,830 mg/l was found to be 20-30 mg/l.

TABLE 9. EFFECT OF VARYING DOSAGES OF NALCOLYTE 677 ON THE SETTLING OF LIME-PRECIPITATED CHROMIUM HYDROXIDE

Nalcolyte 677 Dosage, mg/l	Sludge Volume After 15 Minutes, ml
10	480
20	425
30	390
40	390
60	390
80	390

FLOTATION OF CHROMIUM HYDROXIDE

Flotation, a unit operation, commonly used to separate suspended solids from a liquid phase (16), is accomplished by introducing fine bubbles of air into the waste to be treated. As bubbles adsorb on the surface of particulate matter, air-solid conglomerates are formed which have a net specific gravity less than that of the liquid phase. This net buoyant force causes the solid particles to float to the surface where the scum collects and is removed by skimming.

The most common type of flotation for suspended solids separation uses dissolved air. Air is dissolved in the waste by subjecting a fraction of recycled clarified effluent to extreme turbulence under a pressure of several atmospheres. The "aerated" recycled waste is then mixed with raw waste at atmospheric pressure. Under this "reduced" pressure, the mixture is supersaturated with air which is released from the mixture in the form of minute bubbles. The rising bubbles attach to solid matter and carry the suspended material to the surface of the flotation chamber while clarified effluent is withdrawn from the bottom of the chamber.

Dissolved air flotation is claimed to offer several advantages over conventional solids separation and thickening equipment. Some of the advantages include:

1) Reduced space requirements

2) Lower capital investment

3) More concentrated sludge

4) Higher surface loading rates

In general, however, when suspended solids levels exceed 1%, other separation methods will likely be more economical (17).

Dissolved air flotation was investigated as an alternative to sedimentation for the thickening of chromium hydroxide sludges precipitated from spent chrome tanning liquor. The experiment was designed to establish the following pertinent design parameters:

1) Flotability of chromium hydroxide

2) Rise rates

3) Air-to-solids ratio

4) Recycle ratio

5) Retention time

Batch flotation tests were conducted using the apparatus shown schematically in Figure 5. Chromium hydroxide sludge was placed in the flotation

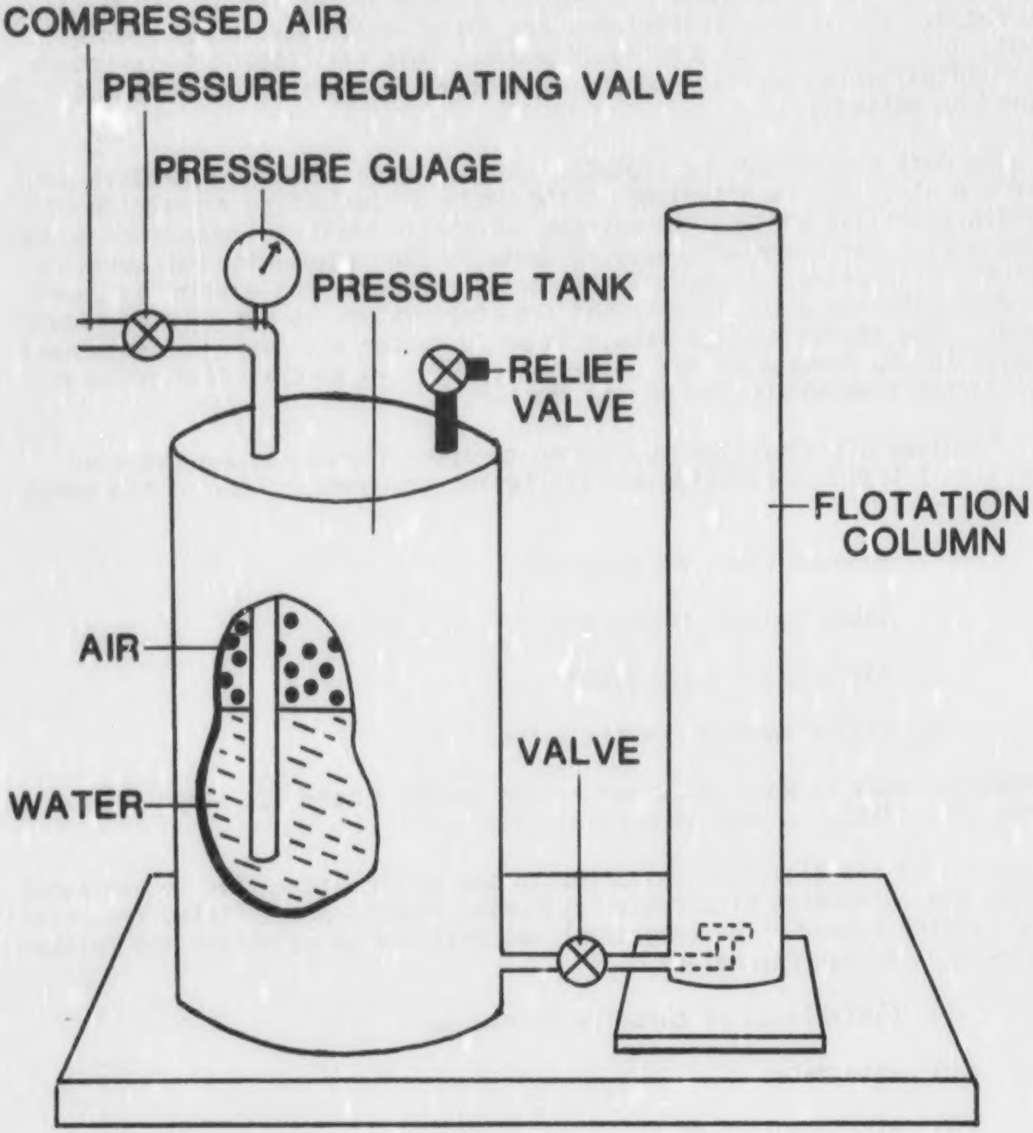
COMPRESSED AIR
PRESSURE REGULATING VALVE
PRESSURE GUAGE
PRESSURE TANK
RELIEF VALVE
FLOTATION COLUMN
AIR
WATER
VALVE

Figure 5: DISSOLVED AIR FLOTATION APPARATUS.

chamber which consisted of an acrylic column having a five inch inside diameter and a height of four feet. An injection port was located two inches from the bottom of the column to introduce pressurized recycle water. A thirty gallon pressure tank was employed for the aeration of recycle water. Compressed air was injected into the bottom of the pressure tank and continuously bled from the top, maintaining a violent turbulent condition within the tank. Pressure within the tank was maintained at 50 psi with a pressure regulating valve located on top of the tank.

In all runs, tap water was employed as the recycle fraction, and was preaerated for a minimum of twenty minutes to insure that the dissolved air concentration approached saturation. The injection of aerated recycle into the flotation column was regulated to give thorough mixing of the two fractions within one to two minutes.

Twelve inches (one gallon) of a soda-ash precipitated chromium hydroxide sludge containing 4,520 mg/l of Cr^{3+} at an optimum pH of 8.5 was placed in the flotation column. The addition of 150% of recycle failed to effect any flotation. In subsequent runs, the addition of up to 600% recycle to one-half gallon of sludge failed to produce an acceptable flotation of the soda-ash precipitated chromium hydroxide.

Similarly, a caustic soda-precipitated sample containing 5,100 mg/l of Cr^{3+} at an optimum pH of 8.8 was tested. Addition of up to 1,000% recycle failed to effect flotation. While flocculation could be enhanced slightly by the addition of flocculants, there was no change in the flotation results at the 10 to 1 recycle ratio.

According to Eckenfelder and O'Connor (18), tap water saturated under 50 psi at room temperature has the potential to release 5.8×10^{-4} pounds of air per gallon when returned to atmospheric pressure. Assuming that the air release was equivalent to that demonstrated by Eckenfelder, the caustic soda-precipitated chromium hydroxide which contained 28,000 mg/l of suspended solids was subjected to an air-to-solids ratio of:

$$\frac{A}{B} = \frac{5.8 \times 10^{-4} \text{ lb/gal} \times 2.5 \text{ gal}}{28{,}000 \text{ mg/l} \times 2.21 \times 10^{-6} \text{ lb/mg} \times 3.78 \text{ l/gal} \times 0.25 \text{ gal}}$$

$$\frac{A}{B} = 0.025 \text{ lb air/lb solids}$$

Therefore, if the dissolved air flotation of caustic soda-precipitated chromium hydroxide in spent chrome tanning liquors is possible, air-to-solids ratios in excess of 0.025 lb air/lb solids must be employed. At a recycle ratio of 1,000%, however, the design requirements are prohibitive. It was concluded, therefore, that dissolved-air flotation of chromium hydroxide is not a viable alternative for solids separation in the recovery of chromium from spent tanning liquors.

A second alternative for the flotation of chromium hydroxide from spent chrome tanning liquors employs in situ generation of carbon dioxide gas.

A 200 ml sample of spent chrome containing 2500 mg/l of chromium was adjusted to pH 8.7 with 2N soda ash. To this mixture 150 mg/l of Nalcolyte 677 was added. The addition of aluminum sulfate equivalent to 350 mg/l of Al^{3+} lowered the pH to 7.0. The mixture effervesced and flotation of chromium hydroxide occurred. Flocculation was excellent, although the removal efficiency was judged to be poor as the underflow retained the green tint characteristic of hydrated, trivalent chromium salt solutions.

The bubbles of carbon dioxide generated during the addition of an acidic aluminum sulfate solution apparently adhere to the floc particles in the same manner as in dissolved-air flotation.

Finally, a third alternative for the flotation of chromium hydroxide by precipitate flotation has been demonstrated by Bhattacharyya et al. (19) Chromium removals of 97% efficiency from chromium (III) hydroxide suspensions containing 0.93 millimoles of Cr per liter (48 mg/l Cr) were obtained by the addition of sodium dodecylsulfate, an anionic surfactant, at a mole ratio of surfactant-to-chromium of 1 to 10.

While these results indicate that precipitate flotation of chromium hydroxide from extremely dilute spent chrome by an anionic surfactant such as sodium dodecylsulfate may be possible, the high concentrations of chromium present in "normal" spent chrome liquors (commonly 5000-7000 mg/l) prevent direct comparison.

SETTLING OF CHROMIUM HYDROXIDE

Laboratory studies proved conclusively that calcium hydroxide used in conjunction with Nalcolyte 677 gave the most efficient precipitation of chromium from spent tanning liquors.

To produce reliable data, useful for the design of a basin for settling lime-precipitated chromium hydroxide, further investigations were carried out in a 5 inch diameter x 48 inch high acrylic column. The settling experiments were designed to determine the effect of chromium and suspended solids concentration on the design overflow rate for clarification and sludge feed rate for thickening.

For each run an appropriate volume of concentrated spent chrome was diluted to 3.0 gallons and the temperature was adjusted to 90°F. The pH of the solution was raised to 9.0 with hydrated lime. The chromium hydroxide slurry was then transferred to the acrylic column. Nalcolyte 677 was added by injecting the polymer through a 1/4" glass tube to the bottom of the acrylic column at a dosage of 50 mg/l. Air was injected through the same tube for two minutes to effect a rapid-mixing. Slow-mixing was achieved by gently stirring the mixture for another 5 minutes. At this point, the liquid height in the acrylic column was slightly greater than 30 inches. While stirring, with the mixture fully suspended, a sample was withdrawn from a sampling port 12 inches from the bottom of the column, and the liquid was drained to the 30 inch level. The floc was allowed to settle under quiescent conditions. After 90 minutes, a sample of the supernatant liquid was withdrawn from a port

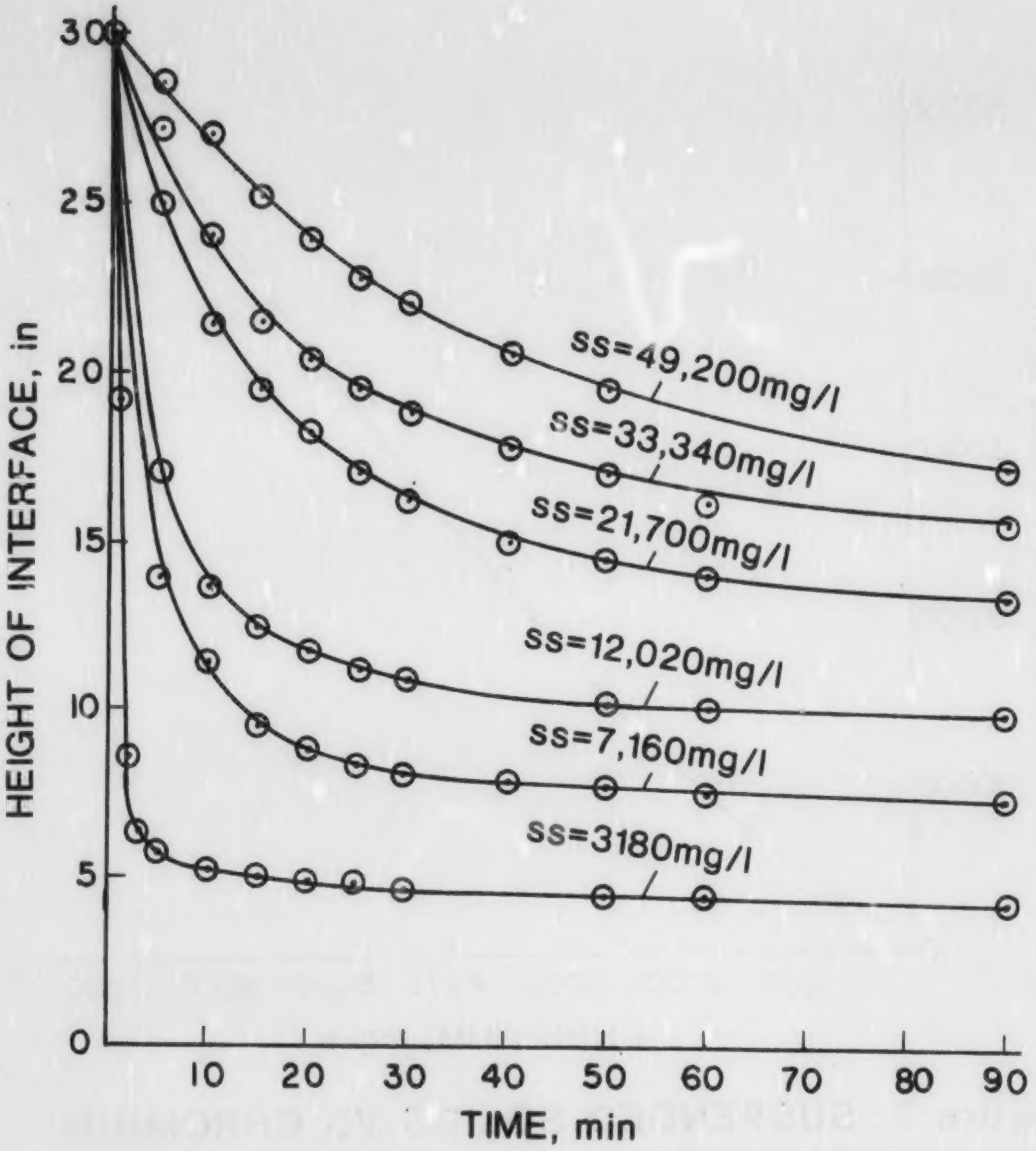

Figure 6: SETTLING OF LIME-PRECIPITATED CHROMIUM HYDROXIDE.

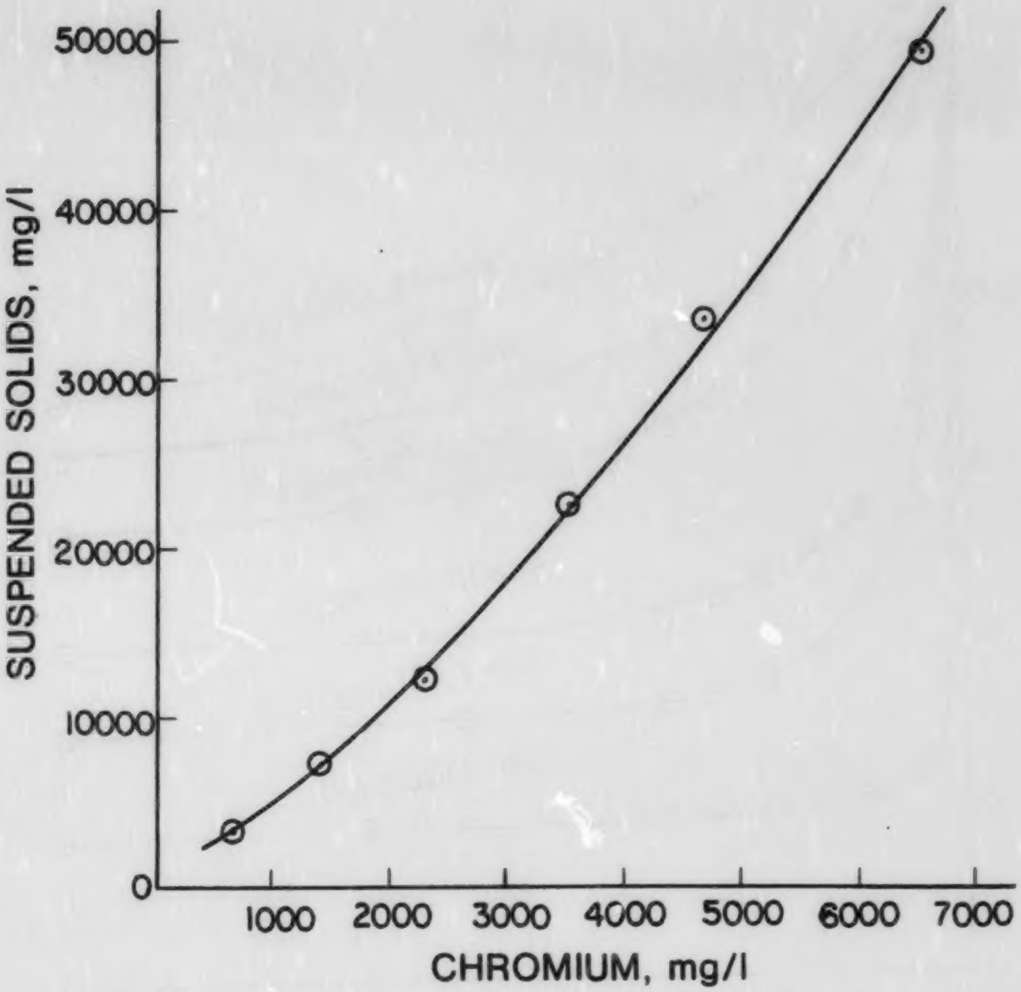

Figure 7: SUSPENDED SOLIDS VS CHROMIUM FOR LIME-PRECIPITATED CHROMIUM HYDROXIDE.

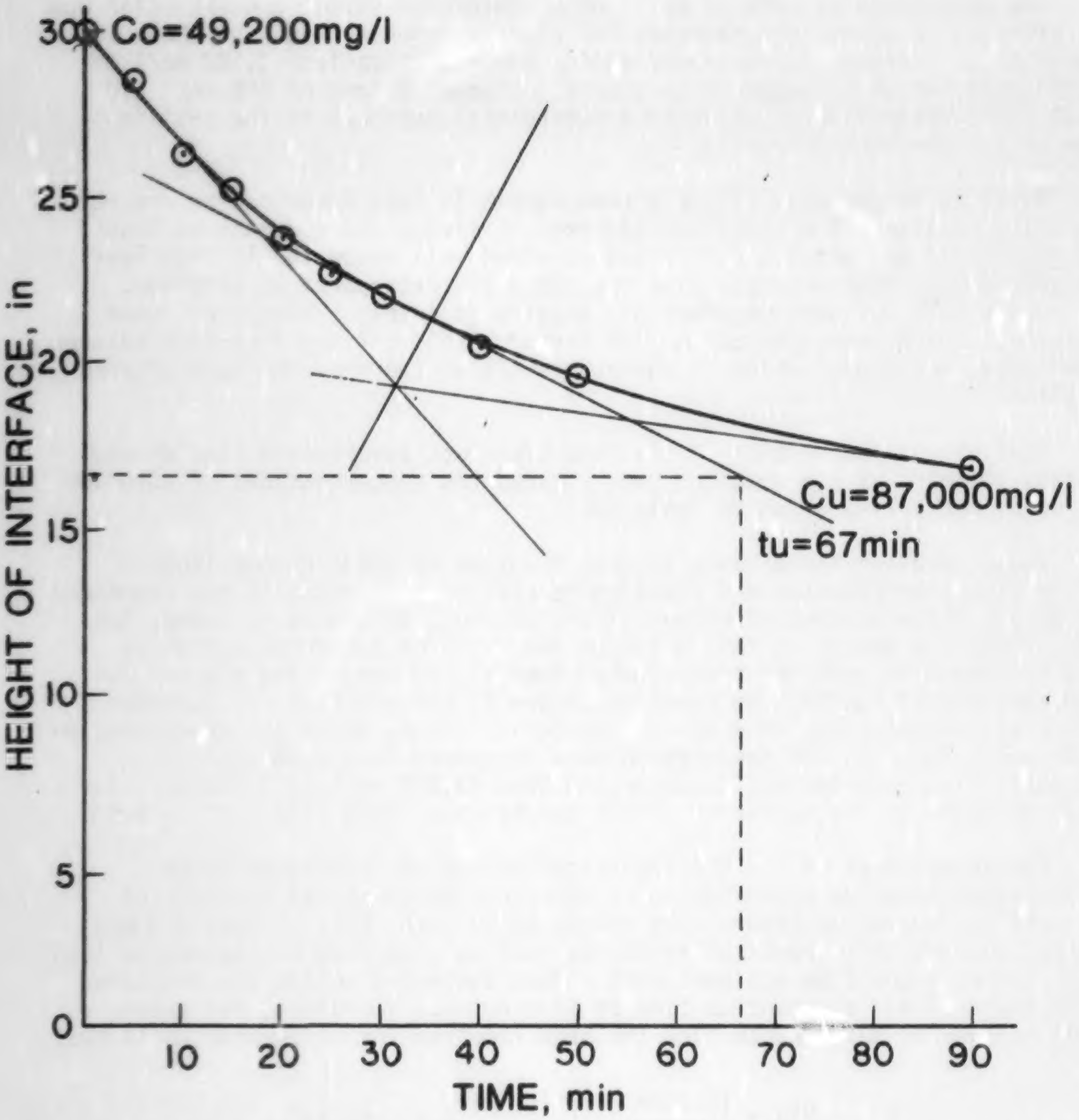

Figure 8: GRAPHICAL DETERMINATION OF THE RATE OF SUBSIDENCE AND THICKENER RETENTION TIME.

at the 24 inch level. Likewise, a sample of the sludge was taken after decanting the supernatant liquid. All three of these samples were analyzed for chromium and for suspended solids.

The dependence of rate of settling on suspended solids concentration and therefore on chromium concentration was clearly demonstrated. As shown in Figure 6, an increase in suspended solids concentration from 3,180 mg/l to 49,200 mg/l, which corresponds to chromium concentrations of 650 mg/l and 6,590 mg/l, respectively, effected a substantial decrease in the settling rate of the chromium hydroxide.

Settling in the most dilute chrome sample is best described as discrete particle settling. The interface between the sludge and supernatant liquid was poorly defined until the floc had subsided well below the 15 inch level. The second most dilute sample also resembled discrete particle settling, although a well defined interface did develop at a column height of about 25 inches. More concentrated samples formed a well defined interface between supernatant and sludge which is characteristic of the hindered type of zone settling.

Analysis of the samples of the feed slurries, supernatant liquids and sludges for each of the settling runs yielded the concentrations of chromium and suspended solids shown in Table 10.

These settling tests revealed that dilution of spent chrome liquor before lime-precipitation and settling results in a decrease in the suspended solids and chromium concentrations of the sludge. It should be noted, however, that as a result of this dilution the ratio of suspended solids to chromium found in both the precipitated feed slurry and in the sludge also decreased significantly. As shown in Figure 7, the plotting of suspended solids vs. chromium yields a non-linear curve. Thus, while the concentration of chromium found in the feed-precipitate decreased from 6,590 mg/l to 650 mg/l, the suspended solids decreased from 49,200 mg/l to 3,180 mg/l for a 35% decrease in the suspended solids-to-chromium ratio from 7.47 to 4.90.

The areas required for the clarification and thickening of lime-precipitated chromium hydroxide were determined by graphical analysis of the settling curves in Figure 6 as described by Rich (20). Figure 8 demonstrates through this graphical technique that an underflow concentration (C_u) of 87,400 mg/l could be achieved with a feed suspended solids concentration of 49,200 mg/l and a retention time of 67 minutes. Therefore, for every 1,000 gallons of daily waste flow the area required for thickening would be:

$$A = \frac{q t_u}{Z_o'} = \frac{(0.0928 \text{ cfm})\ (67 \text{ min})}{2.5 \text{ ft}} = 2.50 \text{ ft}^2$$

where:

A = area in ft^2

q = flow in cfm

t_u= retention time in minutes

Z_o'= depth of column in feet

A thickener to concentrate the slurry to a sludge containing 87,400 mg/l, therefore, would require a surface area of 2.50 ft^2 per 1,000 gallons/day.

From Figure 8 the initial rate of subsidence was calculated by determining the slope of the settling curve near time zero. At a feed suspended solids concentration of 49,200 mg/l an initial rate of subsidence of 0.0252 ft/min was observed. Therefore, for every 1,000 gallons of daily waste flow the area required for clarification would be:

$$A = \frac{q_o}{u} = \frac{(437 \text{ gal/day})}{(1{,}440 \text{ min/day})\ (7.48 \text{ gal/ft}^3)\ (0.0252 \text{ ft/min})}$$

$$A = 1.61 \text{ ft}^2$$

where:

A = surface area in ft^2

q_o= liquid overflow rate in cfm

u = rate of subsidence in ft/min

The area required for clarification was significantly less than that required for thickening. The sludge obtained from clarification should, therefore, be considerably less concentrated than that obtained from thickening. Maximum concentration is important both from the standpoint of optimizing sludge dewatering equipment and subsequent reprocessing of the chromium hydroxide. Thus, the area determined for sludge thickening was used for the design of a settling basin to concentrate chromium hydroxide.

Surface area requirements for each of the six dilutions are illustrated in Table 11 along with other relevant design parameters.

The decreases in chromium concentration by dilution effected a marked increase in the rate of subsidence of the precipitated chromium hydroxide. A tenfold decrease in the chromium concentration from 6,590 mg/l to 650 mg/l resulted in a fiftyfold increase in the settling rate of the resulting

TABLE 10. CHROMIUM AND SUSPENDED SOLIDS CONCENTRATIONS FOR THE SETTLING OF LIME-PRECIPITATED CHROMIUM HYDROXIDE

Feed		Sludge		Supernatant	
Cr	SS	Cr	SS	Cr	SS
6,590	49,200	12,700	87,400	3.74	151
4,650	33,340	9,700	64,120	4.50	120
3,490	21,700	7,700	44,500	2.98	126
2,230	12,020	5,580	31,600	0.84	162
1,330	7,160	5,040	25,220	4.36	114
650	3,180	4,610	20,960	1.96	129

All units mg/1.

TABLE 11. SURFACE AREA REQUIREMENTS FOR THE THICKENING AND CLARIFICATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE AT VARIOUS CHROMIUM AND SUSPENDED SOLIDS CONCENTRATIONS (PER 1000 GALLONS OF DAILY WASTE FLOW)

Cr, mg/l	SS, mg/l	t_u, min	q_o, cfm	u, ft/min	clarification area, ft^2	thickening area, ft^2
6,590	49,200	67	0.0475	0.0252	1.61	2.50
4,650	33,340	44	0.0516	0.0549	0.940	1.64
3,490	21,700	30	0.0546	0.0985	0.565	1.12
2,230	12,020	16	0.0646	0.390	0.168	0.60
1,130	7,160	14	0.0736	0.568	0.130	0.52
650	3,180	8.5	0.0895	1.04	0.082	0.32

chromium hydroxide. Likewise, the same decrease in chromium concentration effected an 88% decrease in the design sludge thickening area requirement, from 2.50 ft^2 to 0.32 ft^2 for each 1,000 gallons per day of feed volume.

The significance of these thickening results are more obvious when expressed in terms of volumetric loadings in gallons of feed per day per square foot of thickener surface area. As shown in Table 12, the design loading is increased from 400 gpd/ft^2 to 3,120 gpd/ft^2 when the chromium concentration of the feed slurry is decreased from 6,590 mg/l to 650 mg/l.

This effect of chromium concentration on the design volumetric loading of a sludge thickening unit is illustrated in Figure 9.

The single most important parameter for the design of a chromium hydroxide sludge thickening unit is the suspended solids loading. The relationship found to exist between suspended solids concentration and the design volumetric loading for chromium hydroxide sludge thickening is shown in Figure 10. Likewise, the relationship between feed suspended solids, retention time and underflow concentration are shown in Figure 11 and Figure 12.

From the practical point of view of collecting and treating spent chrome tanning liquors, the dilutions employed in these settling studies represent concentrations which can be found in a typical spent chrome discharge and the discharge of final wash waters. The influence of the dilution of a spent chrome liquor on several parameters including suspended solids concentration, design volumetric loading, total feed solids, and unit area (thickener surface area required per ton of solids) is illustrated in Table 13.

The effect of the increased volume due to the dilution of spent chrome liquor upon design surface area is offset by the observed increase in settling rates. These data reveal that the net change in surface area requirement is related to the decrease in total feed solids with increased dilution. Within the hindered settling-suspended solids range as chromium was diluted from 6,590 mg/l to 2,230 mg/l, a decrease in total feed solids of approximately 28% from 408 lb/day to 295 lb/day was noted (Figure 13) while the unit area remained constant at an average of 12.1 ft^2/ton-day. The net effect of this dilution was a 29% decrease in the surface area requirement for settling from 2.50 ft^2 for 1,000 gpd at a chromium concentration of 6,590 mg/l to 1.77 ft^2 for approximately 3,000 gpd at a chromium concentration of 2,230 mg/l.

VACUUM FILTRATION OF CHROMIUM HYDROXIDE

In tannery practice, chrome liquors are commonly used at stock concentrations ranging from about 1.0 to 2.0 pounds of Cr_2O_3 per gallon (0.68 to 1.37 pounds of Cr per gallon). The highest concentration of lime-precipitated chromium hydroxide sludge demonstrated after bench-scale thickening contained only 0.106 pounds of Cr per gallon, whereas the most dilute contained only 0.038 pounds per gallon. Sludge concentrations using other alkalis for precipitation were even lower. Further concentration is necessary for subsequent processing of the recovered chromium salt.

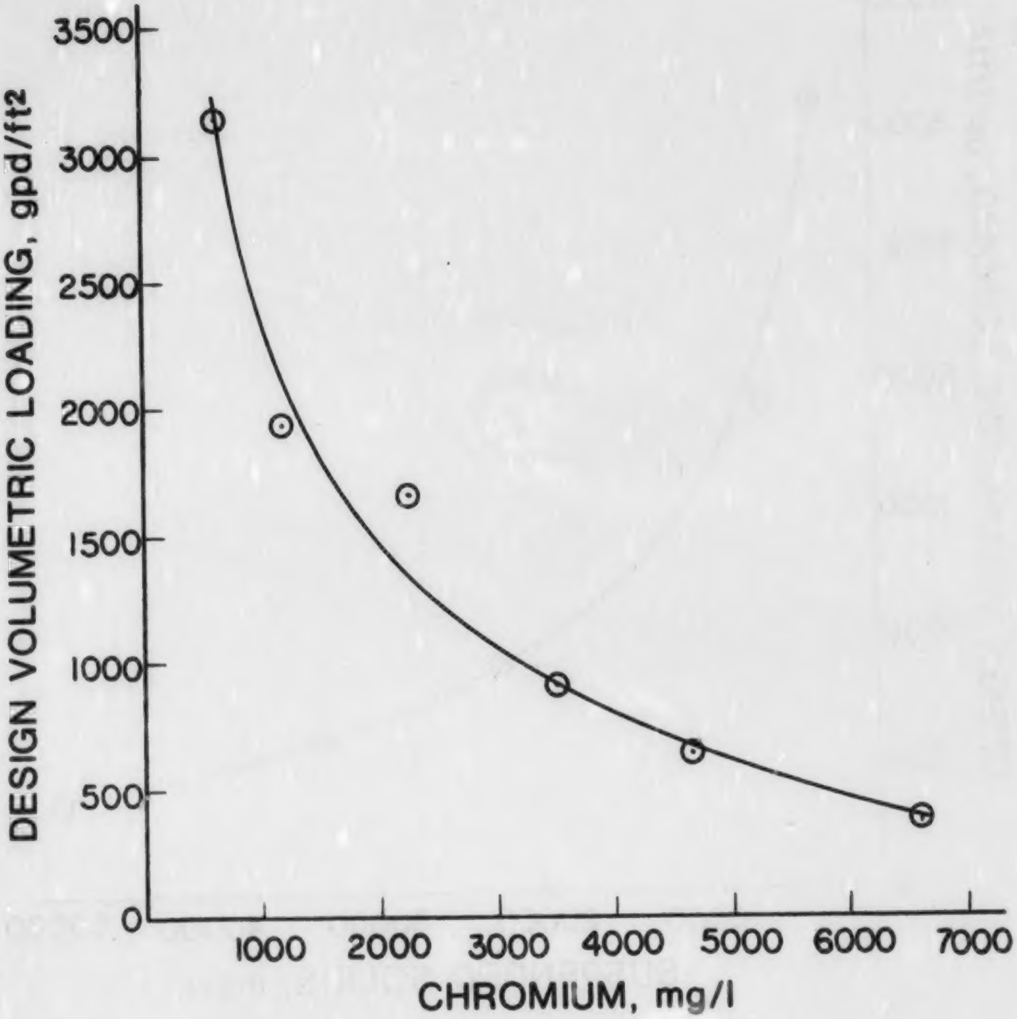

Figure 9: **EFFECT OF CHROMIUM CONCENTRATION ON DESIGN VOLUMETRIC LOADING.**

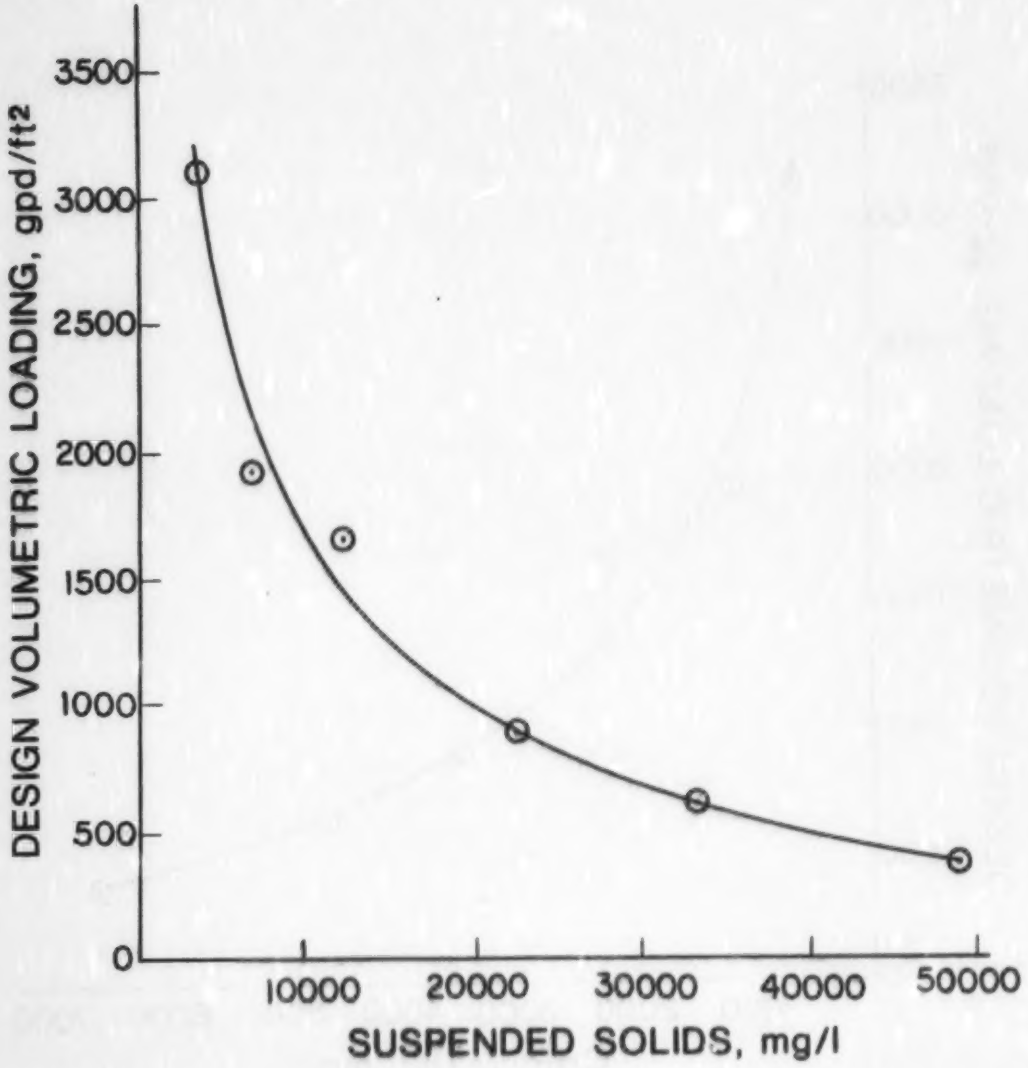

Figure 10: EFFECT OF SUSPENDED SOLIDS CONCENTRATION ON DESIGN VOLUMETRIC LOADING.

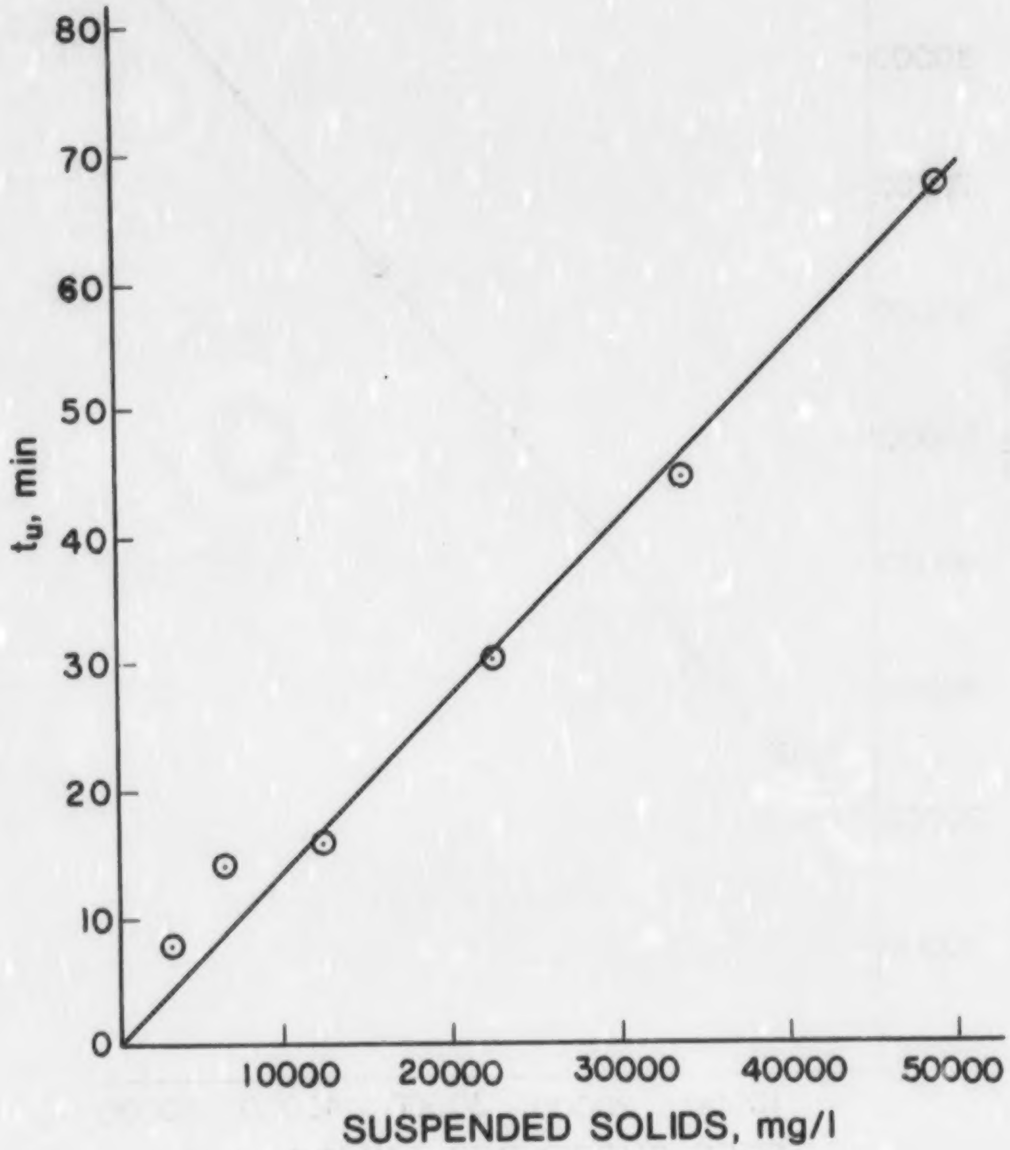

Figure 11: **EFFECT OF SUSPENDED SOLIDS CONCENTRATION ON RETENTION TIME.**

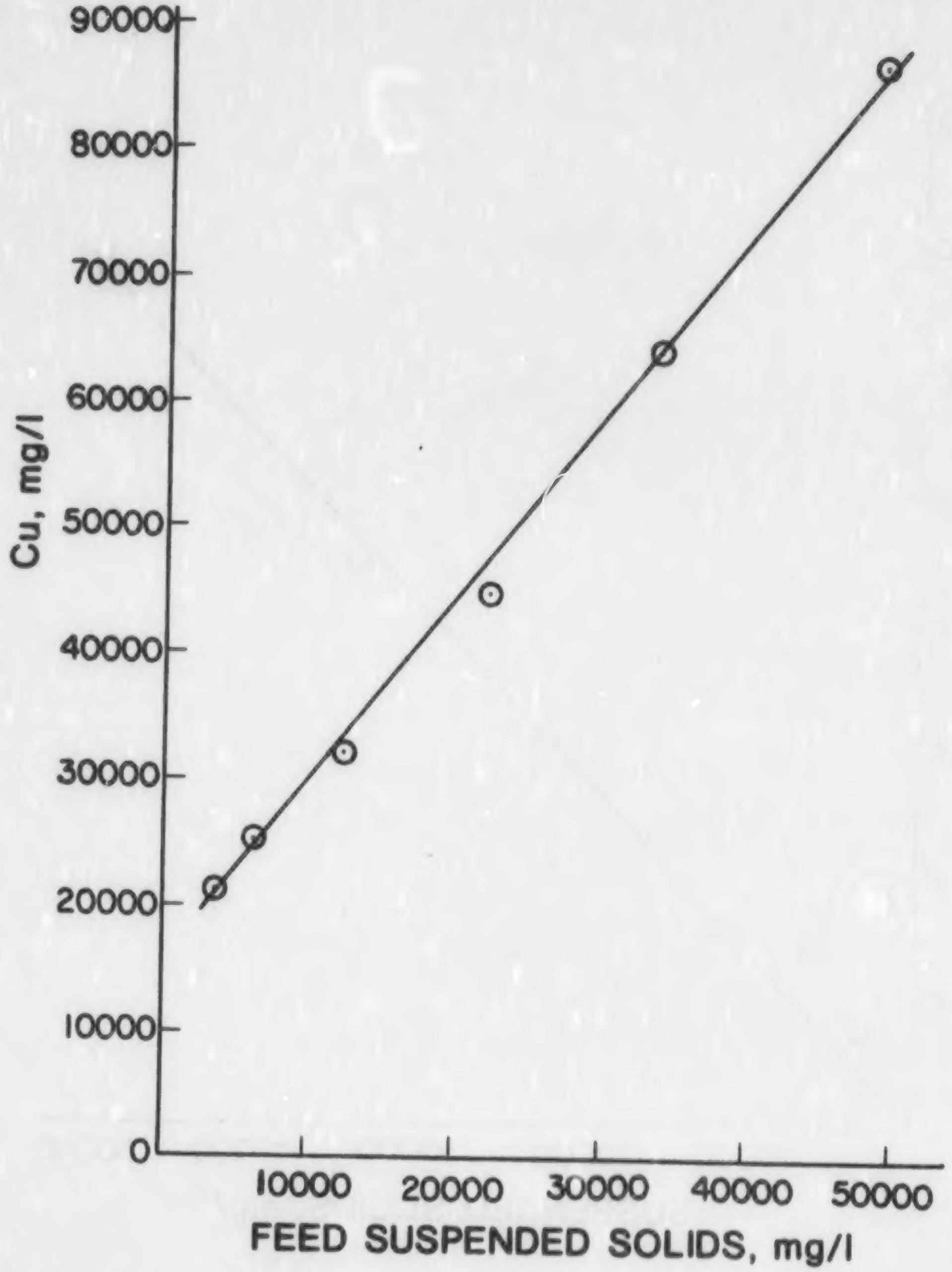

Figure 12: **EFFECT OF FEED SUSPENDED SOLIDS CONCENTRATION ON UNDERFLOW CONCENTRATION.**

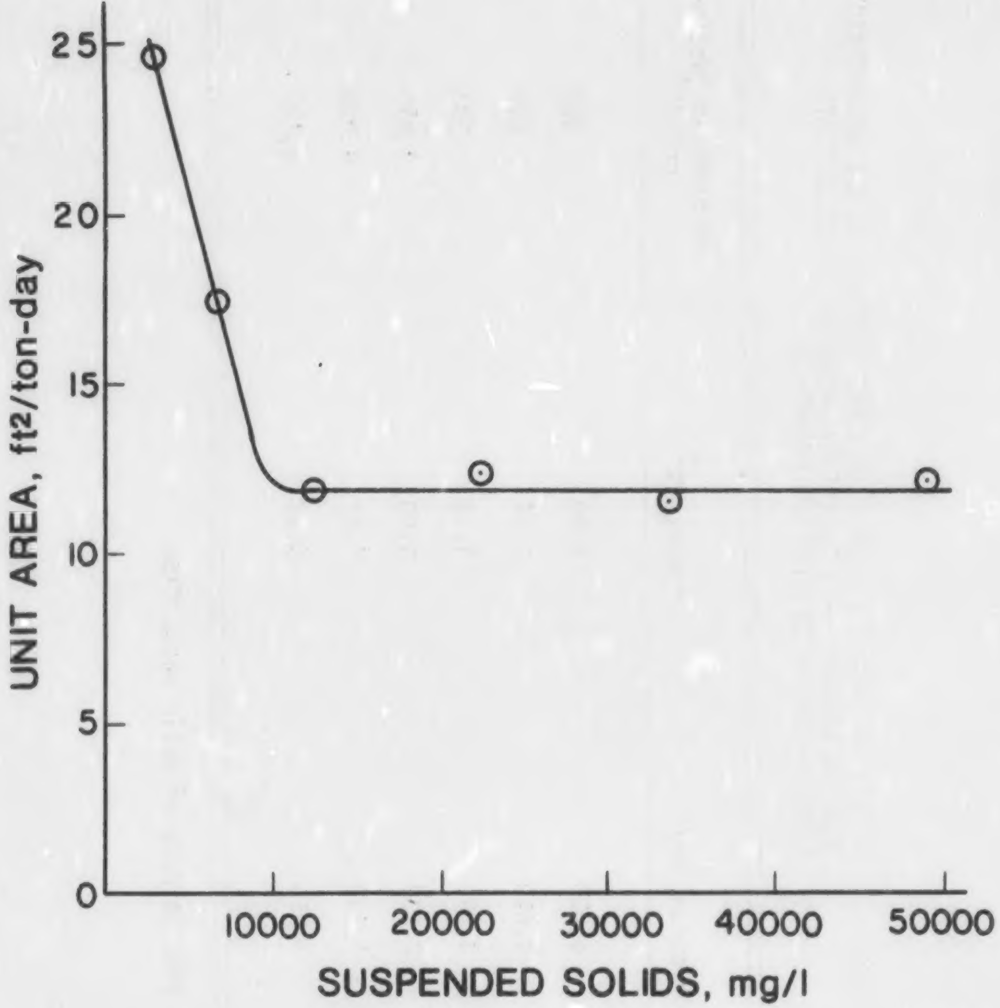

Figure 13: EFFECT OF SUSPENDED SOLIDS ON UNIT AREA.

TABLE 12. EFFECT OF CHANGE IN CHROMIUM CONCENTRATION ON THE VOLUMETRIC SURFACE LOADING OF A THICKENER DESIGNED TO CONCENTRATE LIME-PRECIPITATED CHROMIUM HYDROXIDE

Chromium, mg/l	Area*, ft^2	Volumetric loading, gpd/ft^2
6,590	2.50	400
4,650	1.64	610
3,490	1.12	893
2,230	0.60	1,670
1,130	0.52	1,920
650	0.32	3,120

* Area per 1000 gal/day of daily waste flow

TABLE 13. EFFECT OF DILUTION ON SEVERAL SIGNIFICANT PARAMETERS FOR THE DESIGN OF A CHROMIUM HYDROXIDE SLUDGE THICKENER

Volume, gpd	Chromium mg/l	SS, mg/l	Design Volumetric Loading gpd/ft^2	Area, ft^2	Total Feed SS, lb/day	Unit Area, ft^2/ton-day
1,000	6,590	49,200	400	2.50	408	12.2
1,420	4,650	33,340	610	2.33	394	11.8
1,890	3,490	21,700	893	2.12	342	12.4
2,950	2,230	12,020	1,670	1.77	295	12.0
5,820	1,130	7,160	1,920	3.03	347	17.5
10,100	650	3,180	3,120	3.24	267	24.4

Dewatering of chromium hydroxide sludges by filtration has been reported by several researchers (8, 9, 11, 13). Pressure filtration offers the advantage of high pressure differentials, while vacuum filtration is more amenable to continuous automated operation and can usually be employed at lower capital costs.

The feasibility of vacuum filtration of chromium hydroxide sludges was demonstrated through a series of bench-scale laboratory tests. Initially, Büchner funnel tests were carried out on a spent chrome liquor precipitated with several different alkalis. The apparatus employed in the Büchner tests is shown in Figure 14.

The basic filtration equation presented by Rich (21) is applicable to the Büchner filter test.

$$t/V = \frac{\mu w R'}{2S^2 \Delta p} V + \frac{\mu R_f}{S \Delta p}$$

where t = time, seconds

V = volume of filtrate, ft^3

μ = liquid viscosity, (lb mass)/(ft-sec)

w = weight of dry cake solids per unit of filtrate, (lb force)/(ft^3)

R' = specific resistance, sec^2/lb mass

R_f = resistance due to filter media, (lb force)(sec^2)/(lb mass)(ft^2)

S = area of filter cake, ft^2

Δp = permanent pressure drop due to friction, lb force/ft^2

A plot of t/V vs V is a straight line with slope b and intercept a where:

$$b = \frac{\mu w R'}{2S^2 \Delta p} \text{ and}$$

$$a = \frac{\mu R_f}{S \Delta p}$$

Therefore, when the pressure differential, viscosity, filter area and solids content are known, the specific resistance can be obtained from the slope of the filtration curve.

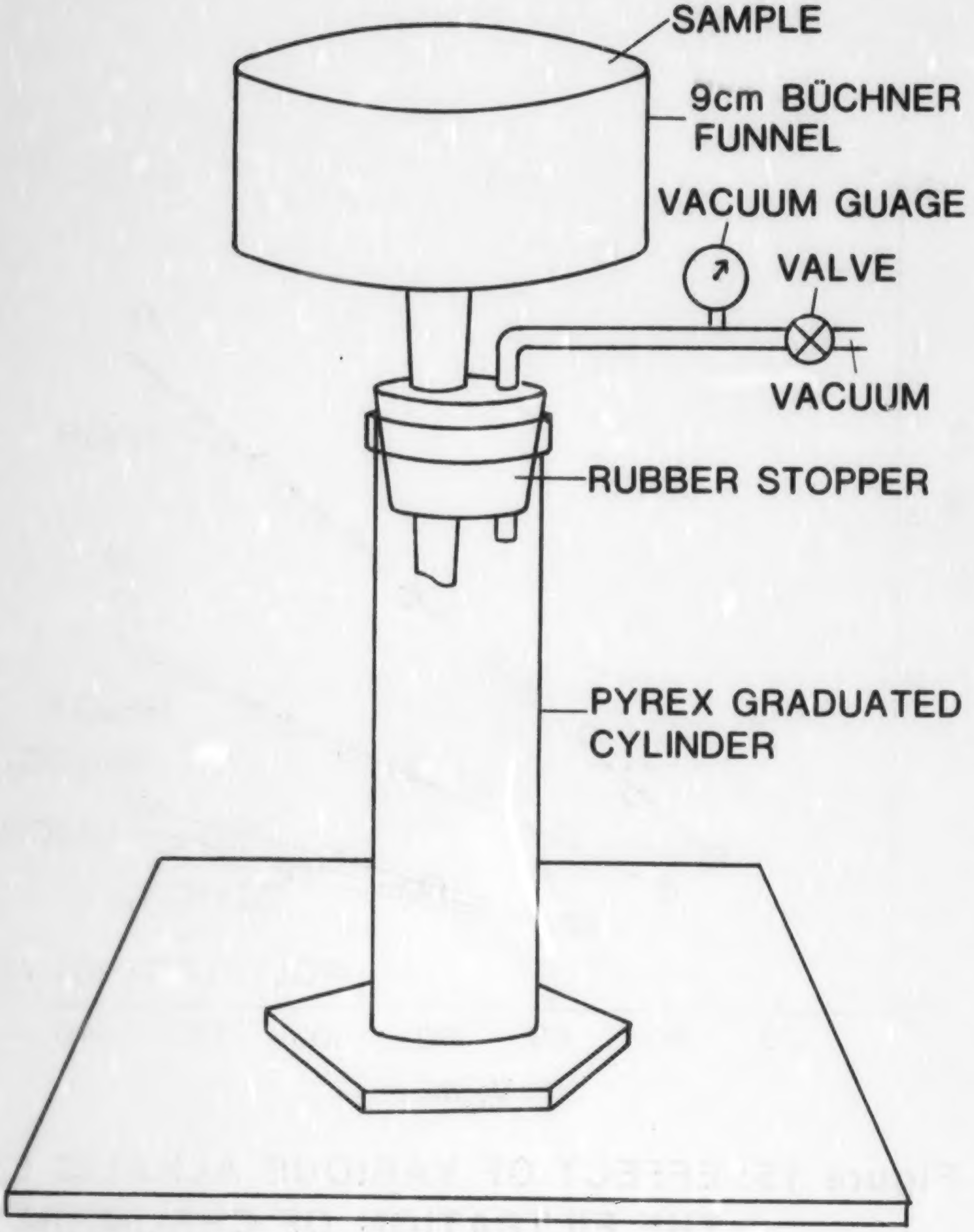
SAMPLE
9cm BÜCHNER FUNNEL
VACUUM GUAGE
VALVE
VACUUM
RUBBER STOPPER
PYREX GRADUATED CYLINDER

Figure 14: BÜCHNER FUNNEL TEST APPARATUS

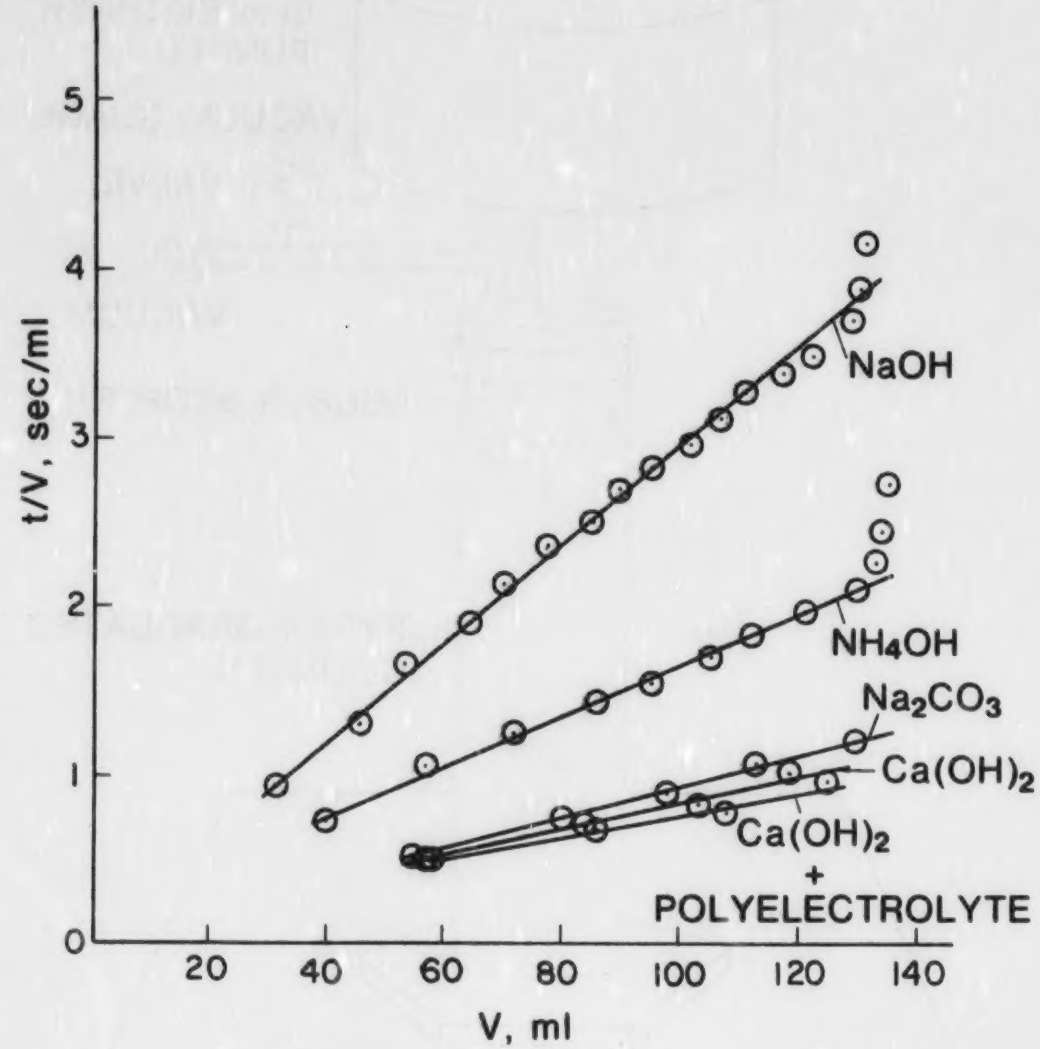

Figure 15: EFFECT OF VARIOUS ALKALIS ON THE FILTRATION OF CHROMIUM HYDROXIDE.

Once the specific resistance has been determined, the filter yield can be predicted by the equation:

$$B = \left[\frac{2\Delta pw\gamma}{\mu R' t_c}\right]^{\frac{1}{2}}$$

where B = filter yield, (lb force)/(ft^2-sec)

γ = fraction of cycle time attributed to cake formation

t_c = time required for one complete filter cycle, seconds

Thus, the specific resistance is directly proportional to the slope of the straight line plot of t/V vs V and the filter yield is inversely proportional to the square root of the specific resistance.

In the Büchner tests, spent chrome was precipitated using an optimum dosage of four different alkalis. The fifth sample was a lime precipitated chromium hydroxide to which 30 mg/l of Nalcolyte 677 was added. After neutralization each of the samples contained 5,120 mg/l of chromium.

A 150 ml sample of each of the sludges was transferred to the Büchner funnel for filtration through Whatman No. 42 filter paper at a pressure differential of 20 inches of mercury. Filtrate volume was measured at 30 second intervals, and the time at which the filter cake began to crack was recorded. The plots of t/V vs V for the several alkalis used are shown in Figure 15. These curves indicate that filtration was markedly affected by changes in the type of alkali used for precipitation.

The values for specific resistance (R') as calculated from the tabulated values for w and b are shown in Table 14. Pressure differential was maintained at 20 inches of mercury and each run was conducted at room temperature. The filter had an area of 7.75×10^{-2} ft^2 and the viscosity for each sample was approximately 5.95×10^{-4} lb mass/ft-sec (0.886 centipoise). Values for the weight of dry cake solids per unit of filtrate (w) were calculated from the corresponding values for feed suspended solids and cake solids and a feed density of 66.2 lb/ft^3 using the equation:

$$w = \frac{pg/g_c}{(1-x)/x - (1-x_c)/x_c}$$

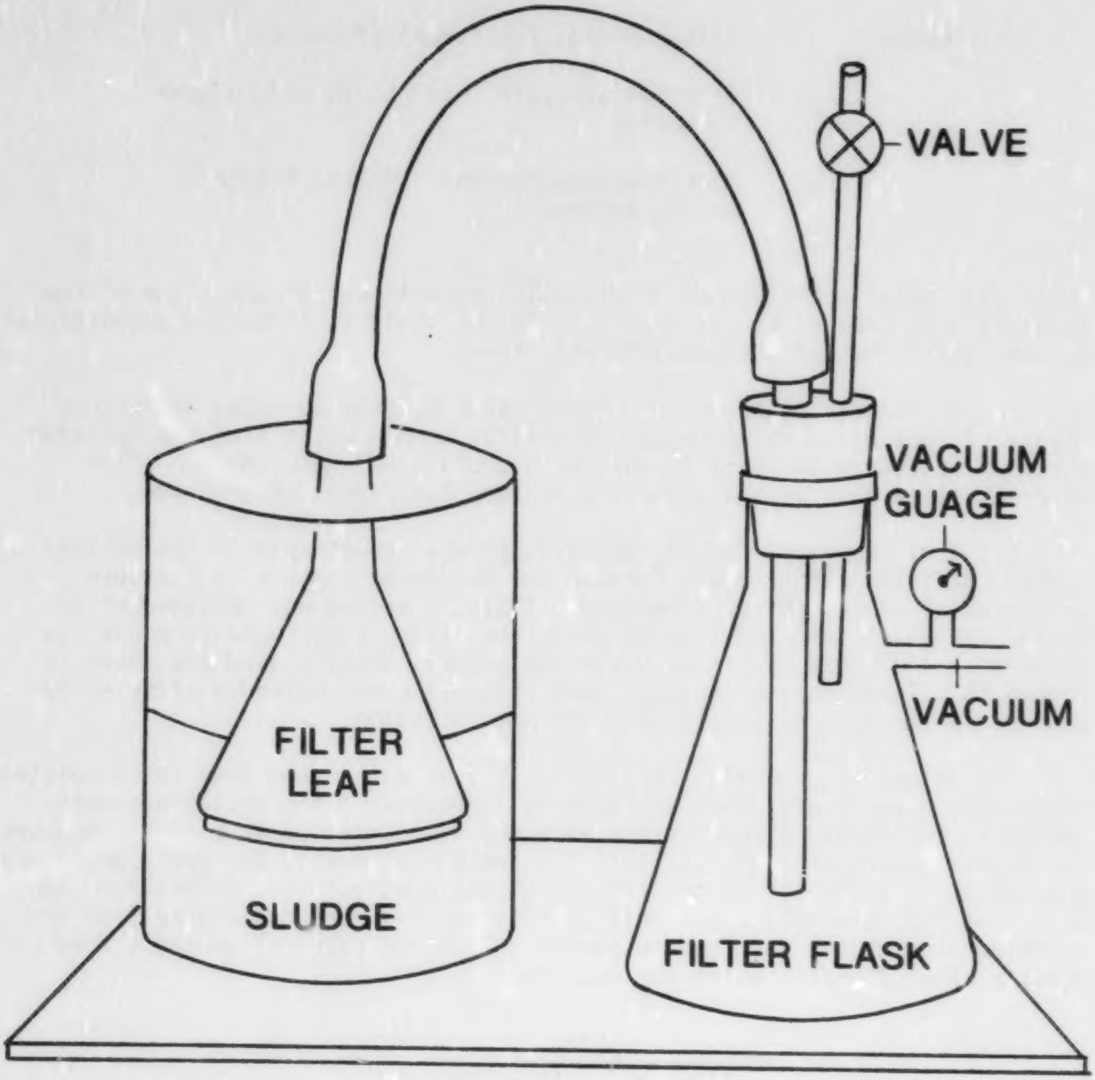
VALVE
VACUUM GUAGE
VACUUM
FILTER LEAF
SLUDGE
FILTER FLASK

Figure 16: FILTER LEAF TEST APPARATUS.

where p = liquid density, lb mass/ft^3

g = acceleration of gravity, ft/sec^2

g_c = Newton's law conversion factor, 32.17 (lb force)/(lb mass)

x = weight fraction of suspended solids in unfiltered sludge.

x_c = weight fraction of suspended solids in filter cake.

The calculated values of filter yield are shown in Table 15. These data confirm that filter yield is highly dependent upon the type of alkali used for precipitation. Thus, by changing from caustic soda precipitation to lime precipitation a 203% increase in filter yield from 0.639 lb/ft^{2-}hr to 1.94 lb/ft^{2-}hr was effected. Likewise, the filtration rate was increased 100% from 2.40 gal/ft^{2-}hr for the caustic soda-precipitated chrome to 4.80 gal/ft^{2-}hr for the lime-precipitated chrome. These increases are due in part to the nearly 50% increase in the feed suspended solids content from 28,000 mg/l for caustic soda to 41,500 mg/l for lime. The resultant filter cake solids increased from 2.5g to 6.4g (dry basis).

The most significant effect of changing the type of alkali was that the area requirements calculated for rotary vacuum drum filtration differ drastically. For example, to filter 1,000 gallons/hour of a lime-precipitated sludge containing 41,500 mg/l of suspended solids a filter area of about 185 ft^2 would be required. If the chromium hydroxide were precipitated by caustic soda, however, the area requirement would be nearly 400 ft^2. Thus, choice of alkali can result in a difference in the design surface area for the vacuum filtration of chromium hydroxide from spent chrome liquors of greater than 100%.

To confirm the results obtained in the Büchner tests and to predict filter yield and filter area requirements more closely, a series of filter leaf tests were carried out on the same sludges used in the Büchner tests. The filter leaf apparatus is shown in Figure 16.

A 400 ml aliquot of each of the sludges was transferred to 1,000 ml pyrex beakers. The filter leaf was fitted with a stainless steel wire gauze over which a Whatman No. 42 filter paper was placed. A vacuum was applied and the filter leaf was positioned beneath the sludge surface. After 150 seconds of cake formation at a vacuum of 20 inches of mercury the leaf was removed and inverted for an additional 150 seconds of dewatering. On a rotary vacuum drum filter this is equivalent to a cycle time of 400 seconds at 37.5% submergence with 25% of the cycle attributed to the cake discharge. The filtrate was collected for each run and its volume measured. The feed volume for each run was measured by difference. The filter cakes obtained were weighed both wet and after overnight drying to obtain filter yields and cake moistures.

TABLE 14. EFFECT OF VARIOUS ALKALIS ON THE FILTRATION OF CHROMIUM HYDROXIDE

Alkali	b, sec/ml^2	Cake solids, %	Feed SS, mg/l	w, lb/ft^3	R′, sec^2/lb mass
NaOH	0.0282	25.7	28,100	1.99	3.20×10^{11}
NH_4OH	0.0150	25.9	25,800	1.82	1.86×10^{11}
Na_2CO_3	0.0086	22.8	31,000	2.16	8.95×10^{10}
$Ca(OH)_2$	0.0077	31.6	41,500	3.03	5.72×10^{10}
$Ca(OH)_2$ + polymer	0.0067	41.2	41,200	2.92	5.17×10^{10}

TABLE 15. EFFECT OF VARIOUS ALKALIS ON FILTER YIELD AND FILTRATION RATE FOR CHROMIUM HYDROXIDE

Alkali	B (filter yield), lb/ft^2-hr	Filtration Rate gal/ft^2-hr
NaOH	0.639	2.40
NH_4OH	0.799	3.22
Na_2CO_3	1.28	4.43
$Ca(OH)_2$	1.94	4.80
$Ca(OH)_2$ + polymer	1.92	4.92

Δp = 20 in Hg

α = 0.375

t_c = 400 sec

$\mu = 0.886 \times 6.72 \times 10^{-4}$ lb/ft-sec

T = 25°C

The results from the filter leaf tests in Tables 16 and 17 confirm that the choice of alkali is indeed a critical factor in the vacuum filtration of chromium hydroxide from spent chrome tanning liquors. Values found for filter yield in these filter leaf tests were slightly higher than the yields predicted in the Büchner tests. Also, filtration rates and sludge feed rates were found to be higher.

The cakes formed by filtration of the caustic soda and ammonium hydroxide-precipitated sludges were each approximately 1.6mm thick and had a pasty consistency which made separation of the cake from the filter paper difficult. The 3.2mm cake formed from the lime-precipitated sludge was separated without difficulty. The soda ash-precipitated sludge yielded a cake which was thicker and easier to discharge than the other sludges but had the highest moisture content at 77.2% H_2O and had the greatest weight per unit volume of sludge filtered.

The filter leaf test simulates the operation of a rotary vacuum drum filter, whereas the Büchner test requires calculation of filter yields from the specific resistance of the various sludges. The authors, therefore, concluded in the face of the observed test result differences that the filter leaf data are the more germane, and should be used in the design of a vacuum filtration system.

It can be concluded from these data that the order of filterability of chromium hydroxide sludges from the various alkalis is: hydrated lime> soda ash> aqueous ammonia> caustic soda.

Several additional factors which can effect filtration include viscosity, pressure differential, suspended solids concentration of the sludge and cake formation time.

In order to test the effect of variation in cake formation time (subsequently translatable to drum speed) on filtration rates, a series of filter leaf tests were conducted in which form time was varied from 44 seconds to 220 seconds (simulating drum speeds of 0.5 rpm to 0.1 rpm, respectively, at 37.5% submergence). A lime-precipitated chromium hydroxide sludge flocculated with Nalcolyte 677, which contained 45,560 mg/l of suspended solids and 7,880 mg/l of chromium was filtered in each run at a temperature of 70°F and under a vacuum of 20 inches of mercury.

The results displayed in Tables 18 and 19 demonstrate that an increase in drum speed increased the rate of filtration and therefore the filter yield. Thus, an increase in drum speed from 0.1 rpm to 0.5 rpm effected an increase in sludge feed rates by over 100% from 6.15 gal/ft^2-hr to 13.4 gal/ft^2-hr. However, there was a corresponding decrease in the cake thickness from 7.2mm at 0.1 rpm to 2.8mm at 0.5 rpm.

As the cake thickness decreased, cake separation from the filter became more difficult. In practice, therefore, the optimum drum speed would be the highest speed which can be utilized without sacrificing good cake discharge. The vacuum filter leaf tests indicated that filter cake formed from the filtration of lime-precipitated chromium hydroxide sludge should be

TABLE 16. FILTER LEAF TEST RESULTS - PART I

Alkali	Feed SS,mg/l	Filtrate vol.,ml	Feed vol.,ml	Wet cake wt.,g	Cake moisture,%
NaOH	28,100	87	95	9.58	74.3
NH_4OH	25,300	130	140	12.56	74.1
Na_2CO_3	31,000	153	173	24.40	77.2
$Ca(OH)_2$	41,500	158	175	19.50	68.4
$Ca(OH)_2$ + polymer	41,200	163	180	19.14	58.8

TABLE 17. FILTER LEAF TEST RESULTS - PART II

Alkali	Filter yield, lb/ft^2-hr	Filtration rate, gal/ft^2-hr	Feed rate, gal/ft^2-hr
NaOH	0.588	2.98	3.22
NH_4OH	1.02	4.47	4.81
Na_2CO_3	1.60	5.26	5.70
$Ca(OH)_2$	1.77	5.45	6.01
$Ca(OH)_2$ + polymer	2.26	5.60	6.18

TABLE 18. EFFECT OF VARIATION IN DRUM SPEED ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE - PART I

Drum speed, rpm	Form time, sec	Dewater time, sec	Crack time, sec	Filtrate volume, ml	Cake thickness, mm	Wet cake weight, g	Dry cake solids, %
0.500	44	48	21	109	2.8	23.0	27.4
0.333	66	72	16	149	4.0	28.8	26.2
0.250	88	96	20	173	4.8	30.9	27.7
0.200	110	120	25	197	4.8	36.0	26.8
0.167	132	144	22	215	5.6	41.2	25.6
0.125	176	192	30	250	6.4	50.6	23.4
0.100	220	240	35	274	7.2	53.6	27.4

Area of filter leaf = $7.75 \times 10^{-2} ft^2$

TABLE 19. EFFECT OF VARIATION IN DRUM SPEED ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE - PART II

Drum speed, rpm	Filter yield, lb/ft^2-hr	Filtrate volume, gal/ft^2-hr	Feed volume, gal/ft^2-hr
0.500	6.03	12.2	13.4
0.333	4.82	10.2	11.2
0.250	4.09	8.85	9.74
0.200	3.70	8.06	8.87
0.167	3.37	7.35	8.09
0.125	2.84	6.38	7.02
0.100	2.79	5.59	6.15

satisfactorily discharged at a thickness as low as 4.8mm.

To determine the effect of the suspended solids concentration in the feed on the vacuum filtration of chromium hydroxide sludges, the filter leaf tests were repeated at 0.2 rpm and 0.1 rpm using a lime-precipitated sludge which contained 30,100 mg/l of suspended solids and 5,250 mg/l of chromium. The results of these runs which are shown in Table 20 demonstrate that while cake thickness decreased substantially from 4.8mm to 3.2mm at 0.2 rpm and from 7.2mm to 5.6mm at 0.1 rpm, the lower feed solids effected an increase in filtration rates from 8.06 gal/ft^2-hr to 9.10 gal/ft^2-hr and from 5.59 gal/ft^2-hr to 6.54 gal/ft^2-hr, respectively. The corresponding filter yields dropped from 3.70 lb/ft^2-hr to 2.41 lb/ft^2-hr at 0.2 rpm and from 2.79 lb/ft^2-hr to 1.95 lb/ft^2-hr at 0.1 rpm with the decrease in feed suspended solids.

A fourth variable which was tested for its effect on filtration was temperature. The variation in filtration rates with temperature is attributed to the change in viscosity. The results of a series of Büchner tests conducted on a lime-precipitated sludge containing 45,560 mg/l of suspended solids and 7,880 mg/l of chromium under a vacuum of 20 inches of mercury are shown in Figure 17 and Table 21. By increasing the feed temperature from 66^{o}F to 110^{o}F at a drum speed of 0.125 rpm and at 37.5% submergence, the filter yield was increased 16.7% from 2.34 lb/ft^2-hr to 2.73 lb/ft^2-hr. Likewise, feed rates and filtration rates were increased by 16.7%.

As these data indicate, there is a distinct advantage to processing spent chrome by precipitation and filtration while it is warm. Where the temperature may drop to 70^{o}F or lower, it may even prove economical to preheat the sludge by steam injection or other means prior to filtration.

ACIDIFICATION OF CHROMIUM HYDROXIDE FILTER CAKE

The widest applicable success of any chrome recycle process depends upon being able to produce a basic chromium sulfate which resembles closely the stock chrome solution being used in the tanning process.

The acidification of recovered chromium hydroxide filter cake with concentrated H_2SO_4 yields chrome liquors of significantly variable characteristics depending upon the type of alkali used for precipitation.

Screened spent chrome samples (200 ml) containing 4,300 mg/l of chromium and an acidity of 220 me/l were precipitated to 100% basicity with the various types of alkali and diluted to 250 ml each. After filtration through a Büchner funnel, the filter cakes were recovered and dissolved in concentrated H_2SO_4 to pH 2.5 to 3.3. As shown in Tables 22 and 23, the redissolved cakes showed considerable variation with respect to the parameters of specific gravity, chromium concentration, and residues.

Most significantly, the suspended solids concentration for lime-precipitated chrome was drastically higher than for sodium hydroxide, ammonium hydroxide or sodium carbonate. Calcium sulfate was the principal

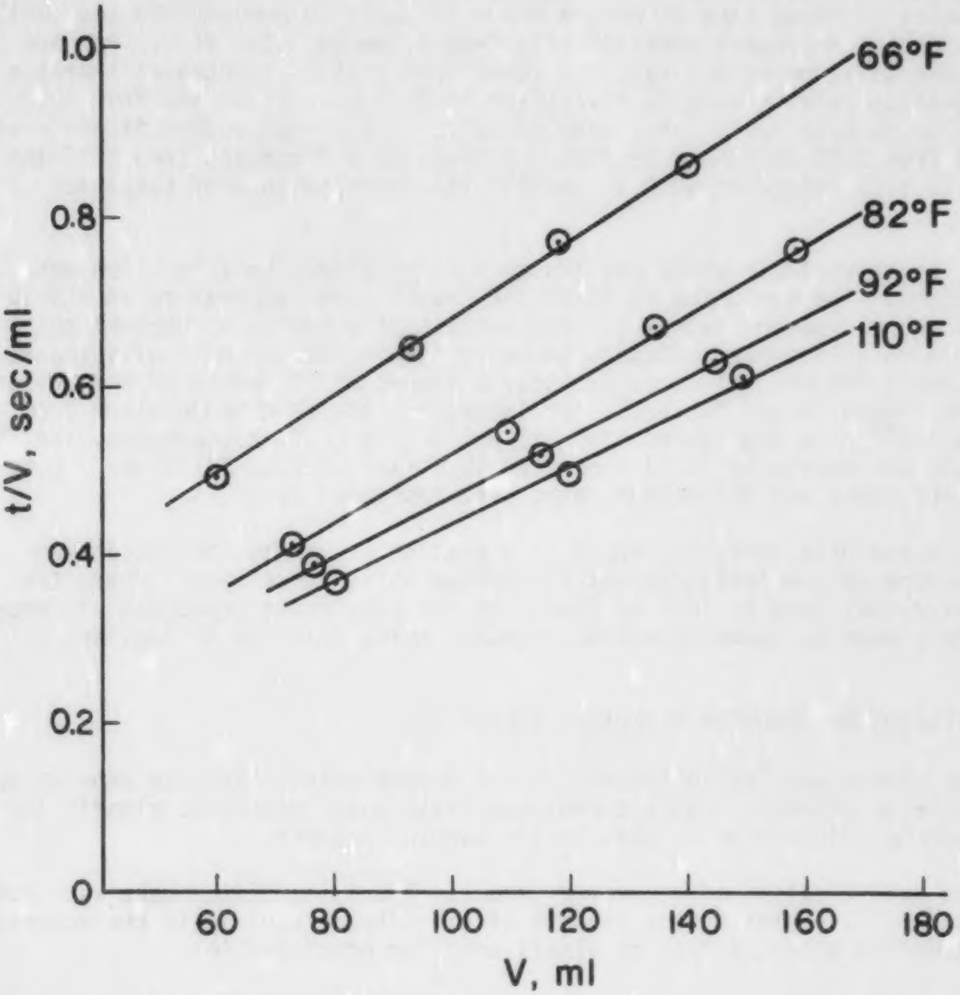

Figure 17: EFFECT OF TEMPERATURE ON THE FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE.

TABLE 20. EFFECT OF VARIATION IN SUSPENDED SOLIDS CONCENTRATION ON THE VACUUM FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE

SS, mg/l	Drum speed, rpm	Wet cake weight, g	Dry cake solids, %	Cake thickness, mm	Filter yield, lb/ft^2-hr	Filtrate volume, gal/ft^2-hr	Feed volume, gal/ft^2-hr
45,560	0.200	36.0	26.8	4.8	3.70	8.06	8.87
30,100	0.200	25.3	24.9	3.2	2.41	9.10	10.0
45,560	0.100	53.6	27.4	7.2	2.79	5.59	6.15
3C,100	0.100	37.6	27.2	5.6	1.95	6.54	7.19

TABLE 21. EFFECT OF TEMPERATURE ON THE FILTRATION OF LIME-PRECIPITATED CHROMIUM HYDROXIDE

Temp, °F	μ, cp	b, sec/ml^2	R', sec^2/lb mass	B, lb/ft^2-hr	Filtrate volume, gal/ft^2-hr	Feed volume, gal/ft^2-hr
66	0.96	0.00461	3.05×10^{10}	2.34	5.57	6.12
82	0.83	0.00412	3.15×10^{10}	2.48	5.91	6.40
92	0.75	0.00345	2.99×10^{10}	2.70	6.43	7.07
110	0.61	0.00339	3.60×10^{10}	2.73	6.51	7.16

$w = 3.14$ lb/ft^3

TABLE 22. ACIDIFICATION OF CHROMIUM HYDROXIDE FILTER CAKE - PART I

Alkali	Volume of redissolved chrome, ml	Sp. Gr.	pH	Cr, mg/l	Cr, lb/gal
NaOH	14.1	1.212	2.80	57,000	0.475
NH_4OH	13.4	1.192	2.50	61,000	0.508
Na_2CO_3	19.3	1.203	3.30	43,000	0.358
$Ca(OH)_2$	16.4	1.244	3.00	49,600	0.408

TABLE 23. ACIDIFICATION OF CHROMIUM HYDROXIDE FILTER CAKE - PART II

Alkali	Total solids, mg/l	Total dissolved solids, mg/l	Suspended solids, mg/l	Cr in Suspended solids, %
NaOH	373,000	346,900	26,100	5.4
NH_4OH	420,000	392,300	27,700	4.3
Na_2CO_3	312,000	292,200	19,800	4.2
$Ca(OH)_2$	441,000	279,000	162,000	1.6

component of these suspended solids. It should be noted that the chromium component of the suspended solids was substantially lower for the lime-precipitated chrome than for other alkalis indicating that there is no gross coprecipitation of chrome with calcium sulfate.

Another important difference is related to the relatively wetter filter cake obtained for the filtration of soda ash-precipitated chromium hydroxide, and therefore the greater volume of redissolved chrome. Thus, soda ash produced a redissolved chrome which was substantially lower in chromium concentration (at 43,000 mg/l) than did the other alkalis. Likewise, total solids and suspended solids were considerably lower.

It was further noted that although the total and suspended solids concentrations for lime-precipitated chrome were substantially higher than when other alkalis were used, the total dissolved solids of 279,000 mg/l were lower than for other alkalis. Therefore, if the calcium sulfate could be conveniently removed, precipitation of this insoluble salt may prove beneficial in that it significantly reduces the non-chromium fraction of dissolved salts present in the re-acidified liquor.

Finally, it is important to point out that these recovered chrome liquors are substantially lower in chrome content than most commercially available tanning agents. Therefore, in order to produce a "standard" tanning concentration of 1 lb/gal of Cr_2O_3 (0.685 lb Cr/gal) it would be necessary (in Pfister & Vogel production) to blend the recovered chrome liquor at a 5 to 4 ratio with a stock chrome liquor of 1.5 lb Cr_2O_3 per gallon (1.03 lb Cr/gal).

PILOT FILTRATION STUDIES

While lab-scale Büchner tests and filter leaf tests can be used to predict optimum filtration conditions and filter area requirements, there are several important factors which must be evaluated on a pilot-scale before full-scale filtration equipment can be specified. These factors include the type of cake discharge mechanism required (i.e., belt, string, scraper or roller discharge, etc.) and filter medium to be employed. Likewise, it is imperative to establish whether blinding of the filter medium might be encountered in full-scale operations. Blinding must always be anticipated in the filtration of wastes containing substantial concentrations of oils, fats and greases.

In pilot-scale filtration studies, a 1' wide by 3' diameter rotary vacuum drum filter was employed. The filter was fitted with a string discharge and a Nylon multi-filament fabric ("Feon" No. WNH-W4IO-SE7) with an air permeability of 5.2 cfm/ft^2 @ 0.5" H_2O. Total filtering area equalled 9.4 ft^2.

Test runs on the pilot filter confirmed the filter area calculations for separation of precipitated chromium hydroxide from spent chrome liquors, as predicted by the laboratory, bench-scale tests. Likewise, during 40 hours of "non-continuous" operation of the filter, the string discharge mechanism and Nylon filter cloth performed satisfactorily with no sign of wear. The animal fats and greases present in our spent chrome liquors did not blind the filter media.

Approximately 100 gallons of spent chrome liquor containing 4,660 mg/l of chromium was precipitated at pH 9.0 with a slurry of hydrated lime and then was flocculated with 30 mg/l of Nalcolyte 677. The precipitated sludge contained 38,440 mg/l of suspended solids. During the filtration run, drum submergence was maintained at 37.5% and drum speed at 0.125 rpm.

As shown in Table 24, at 68°F and under a cake-form vacuum of 22" Hg the sludge was filtered at a rate of 6.0 gallon of filtrate /ft^2-hr. Filter cake was discharged at an average thickness of 3.2mm and an average moisture content of 63%.

TABLE 24. PILOT-SCALE VACUUM FILTRATION OF CHROMIUM HYDROXIDE

	Hydrated lime	Soda ash
pH	9.0	8.7
flocculant	30 ppm Nalcolyte 677	none
suspended solids	38,440 mg/l	23,740 mg/l
temperature	68°F	70°F
feed rate	6.6 gal/ft^2-hr	7.9 gal/ft^2-hr
filtration rate	6.0 gal/ft^2-hr	7.3 gal/ft^2-hr
cake thickness	3.2 mm	5.6 mm
filter yield (wet)	5.7 lb/ft^2-hr	6.8 lb/ft^2-hr
cake moisture	63%	76.4%
filter yield (dry)	2.1 lb/ft^2-hr	1.6 lb/ft^2-hr

drum speed = 0.25 rpm
cake form vacuum = 22" Hg
drum submergence = 37.5%

Soda ash precipitation (with 1 lb/gal soda ash solution) of another 100 gal fraction of the spent chrome liquor yielded a sludge containing 3,890 mg/l of chromium and 23,740 mg/l of suspended solids at a pH of 8.7. At 0.125 rpm, 37.5% submergence and under a cake-form vacuum of 22" Hg, this sludge was filtered at 70°F at a rate of 7.3 gal filtrate/ft^2-hr corresponding to a feed rate of 7.9 gal/ft^2-hr, with a filter yield of 1.6 lb dry solids/ft^2-hr. Cake was discharged at an average thickness of 5.6 mm and contained 76.4% moisture.

During both runs the discharge of cake from the filter by the string mechanism was complete and no significant blinding of the Nylon filter medium was observed. The 3.2 mm cake thickness was judged to be the minimum which can be tolerated for lime-precipitated chromium hydroxide. The 5.6 mm observed for soda ash-precipitated sludge, however, is thicker than the optimum for cake discharge.

Thus, it is apparent that the soda ash-precipitated sludge with its substantially lower solids content can be filtered at a faster volumetric rate than lime-precipitated sludge. However, most of this rate difference is offset by the increased volume of sludge due to the addition of soda ash as a relatively dilute solution.

SEPARATION OF OILS AND GREASES FROM SPENT CHROME LIQUOR

A laboratory-scale, mass-balance evaluation of the filtration of alkali-precipitated chromium hydroxide from spent chrome indicated that the contaminating fats, oils and greases are essentially non-filterable. Spent chrome liquor containing 7,280 mg/l of chromium and 8,820 mg/l of Oil and Grease was precipitated with calcium hydroxide or sodium carbonate to pH 9.0. The sludges were filtered through Whatman No. 42 filter paper on a Büchner funnel, and the filter cakes were dried and redissolved in hydrochloric acid. As shown in Table 25, analyses of the filtrates and the redissolved cakes revealed that less than one percent of the Oil and Grease was recovered in the filtrates.

Therefore, it is apparent that to prevent Oil and Grease build-up to intolerable levels in recycled chrome, they must be separated prior to precipitation and filtration and/or after acidification of the chromium hydroxide filter cake. To search out feasible alternatives for Oil and Grease separation several bench-scale and pilot-scale experiments were conducted.

TABLE 25. REAPPORTIONMENT OF OIL & GREASE DURING THE FILTRATION OF CHROMIUM HYDROXIDE

	Hydrated lime	Soda ash
aliquot	100 ml	100 ml
Oil & Grease	882 mg	882 mg
volume after precipitation	121 ml	121 ml
filtrate volume	106 ml	103 ml
dry cake weight	5.43 g	4.62 g
cake Oil & Grease-dry basis	16.3%	17.1%
cake Oil & Grease	884 mg	791 mg
filtrate Oil & Grease	25.5 mg/l	31.0 mg/l
filtrate Oil & Grease	2.7 mg	3.2 mg

Flotation

A 50 gallon "batch" of spent chrome containing 7,110 mg/l of Oil and Grease was settled for one hour. An aliquot of the underflow contained only 181 mg/l of Oil and Grease, indicating that 97.5% was concentrated in the supernatant layer.

Similarly, reacidified chrome containing 6,820 mg/l of Oil and Grease yielded an underflow containing 990 mg/l, equivalent to an 85.5% transfer into the supernatant, but after 72 hours.

Centrifugation

Centrifugation of a spent chrome liquor containing 12,060 mg/l of Oil and Grease in an International Model SVB laboratory centrifuge for 5 minutes at 1500 rpm yielded an underflow which analyzed at 220 mg/l, indicating that 98.4% of the Oil and Grease was thus separated. Likewise, centrifugation for 5 minutes at 1500 rpm of a reacidified chrome containing 6,820 mg/l of Oil and Grease yielded an underflow containing 1,420 mg/l with 79.3% being transferred to the scum layer.

Extraction

An aliquot of spent chrome liquor which contained 12,060 mg/l of Oil and Grease was sequentially extracted at room temperature with two volumes (25% and 10%) of chloroform. This two-stage, liquid-liquid extraction produced an aqueous phase containing 220 mg/l of Oil and Grease. However, extraction of a reacidified chrome with either chloroform or hexane proved impractical since no discrete separation of the organic solvent phase and the aqueous phase could be obtained.

Adsorption

A 20 ml aliquot of a spent chrome containing 12,060 mg/l of Oil and Grease was passed through a packed column containing 100 c.c. of 3 mm. dia. glass beads. The effluent from the adsorption column analyzed 5,600 mg/l indicating a 53.6% retention. Suspended Oils and Greases and fine fibrous solids had a blinding effect on the column and made regeneration with organic solvent impracticable. Likewise, reacidified chrome containing 6,820 mg/l of Oil and Grease was treated by application to the adsorption column resulting in a 31.4% retention, with the underflow containing 4,690 mg/l of Oil and Grease.

Absorption

Filtration of spent chrome through a column containing 100 cc of blue shavings proved impossible. Once the blue shavings were wetted, the column became completely impervious to spent chrome liquor.

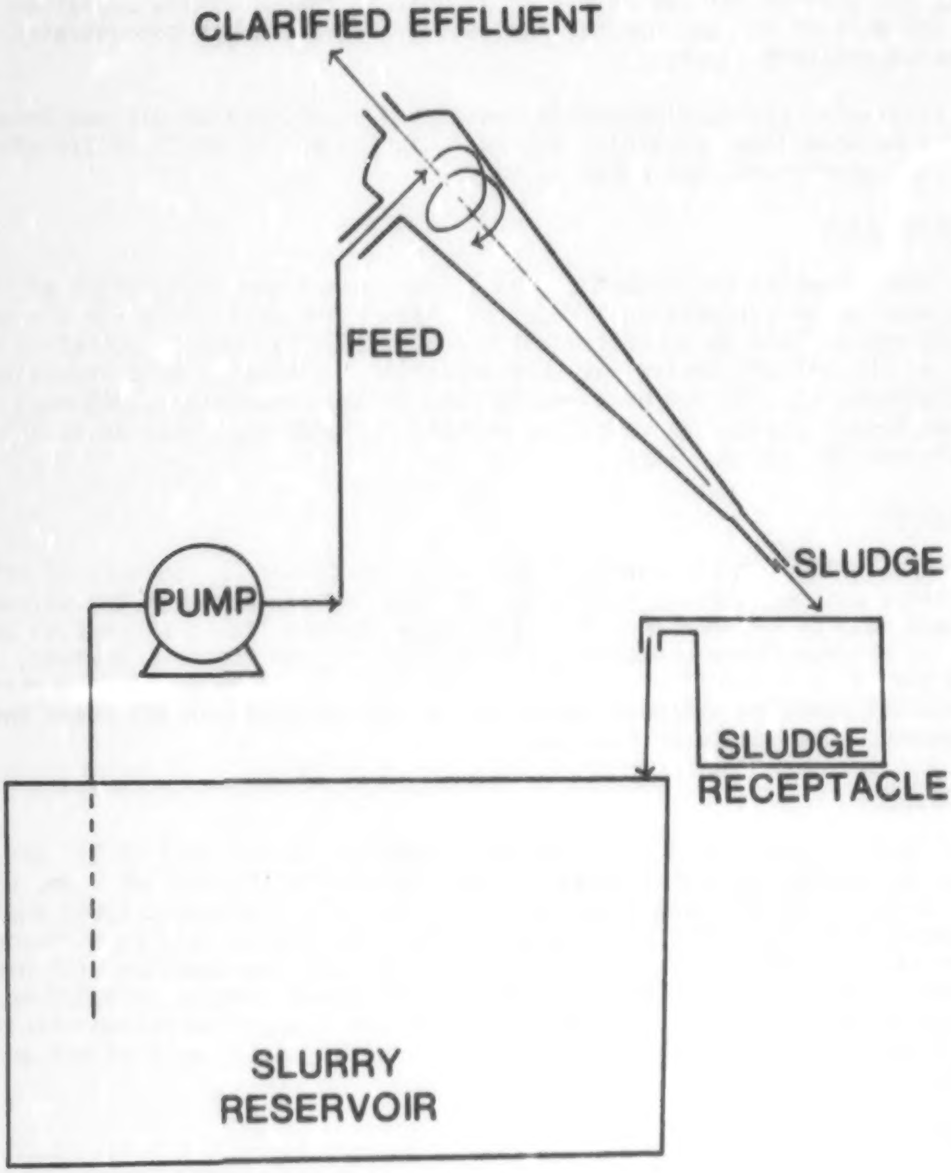
CLARIFIED EFFLUENT
FEED
PUMP
SLUDGE
SLUDGE RECEPTACLE
SLURRY RESERVOIR

Figure 18: HYDROCYCLONIC SEPARATOR.

HYDROCYCLONIC SEPARATION OF CALCIUM SULFATE FROM REACIDIFIED SPENT CHROME

The major disadvantage of using hydrated lime for precipitation in the recovery of chromium from spent chrome tanning liquors has been the formation of calcium sulfate. This sparingly soluble salt forms during the precipitation of the chromium hydroxide and on acidification with H_2SO_4 to regenerate the basic chrome sulfate.

A spent chrome liquor containing 6000 mg/l of chromium, when precipitated at pH 9.5 with hydrated lime followed by reacidification with concentrated sulfuric acid to pH 3.5, yielded a suspension of the rapidly settling insoluble white salt. The suspension analyzed at 43,800 mg/l of suspended solids, of which 31,300 mg/l was fixed suspended solids, primarily calcium sulfate.

It appears, therefore, that sequential recycles through lime-precipitation and acidification of settled sludge with H_2SO_4 would result in an unacceptable build-up of calcium sulfate.

To demonstrate the removal of precipitated calcium sulfate, 50 gallons of calcium sulfate-chrome slurry prepared as above was charged to a hydrocyclonic separator (Bauer Clarifier No. 677-1)(22) depicted schematically in Figure 18.

The hydrocyclonic separator utilizes a centrifugal force many times the force of gravity to remove suspended solids from liquids. A slurry is pumped under controlled pressures into the broad end of a fixed cone in a tangential pattern. The cyclonic flow which develops causes particulate matter to impinge on the wall of the cone and finally discharge through the narrow end while the liquid follows a vortex back up the center of the cone to be discharged through an overflow at the broad end. Thus, grit or other solid matter which is substantially denser than the liquid carrier can be removed quickly using equipment which occupies very little space.

The hydrocyclonic separator employed in this study operates at a feed rate of 22 gpm and has overall dimensions (including pump and reservoir, cyclone, and solids collector) of 31" x 31" x 66" high.

The results of three cyclone runs with varying orifices are shown in Tables 26 and 27. The solids data are for grab samples collected at the cyclone orifice and overflow, and from the main reservoir during operation of the unit. Sludge volumes were determined by mass balance and are expressed as percent of feed volume.

With an orifice diameter of 3/16", and a feed suspended solids concentration of 58,700 mg/l, an effluent containing only 9,770 mg/l of suspended solids was obtained, effecting an 83.4% reduction. The sludge was equivalent to approximately 9% of the feed volume and contained 540,000 mg/l of suspended solids. Likewise, the fixed suspended solids concentration was reduced by 94.5% from 39,100 mg/l in the feed to 2,160 mg/l in the effluent while the sludge fixed suspended solids concentration was 413,000 mg/l.

TABLE 26. CYCLONE SEPARATION OF CALCIUM SULFATE FROM SPENT CHROME LIQUOR AT VARYING ORIFICE DIAMETERS - PART I

Orifice dia., in	Influent SS, mg/l	Effluent SS, mg/l	Sludge SS, mg/l	Sludge vol., %	Removal %
1/8	43,000	10,800	625,000	5.0	75.2
5/32	57,800	9,790	755,000	6.4	83.1
3/16	58,700	9,770	540,000	9.1	83.4

TABLE 27. CYCLONE SEPARATION OF CALCIUM SULFATE FROM SPENT CHROME LIQUOR AT VARYING ORIFICE DIAMETERS - PART II

Orifice dia., in	Influent fixed SS, mg/l	Effluent fixed SS, mg/l	Sludge fixed SS, mg/l	Sludge vol., %	Removal, %
1/8	31,300	4,260	490,000	5.6	86.4
5/32	38,000	2,300	580,000	7.0	93.9
3/16	39,100	2,160	413,000	9.0	94.5

The sludge had a specific gravity of 1.395 and contained 62 ml/100 ml of settleable solids (1 hour). Further analysis of these three fractions indicated that there was a slight disapportionment of chromium, with the effluent being slightly higher in chromium content than the recovered sludge. The feed slurry contained 5,620 mg/l of chromium while the effluent contained 5,700 mg/l and the sludge 5,030 mg/l. Therefore, the solids thus redistributed from the feed slurry to the sludge fraction are non-chromium suspended solids.

The successful application of the cyclone for the separation of calcium sulfate from spent chrome liquors suggested that the calcium sulfate which is precipitated during the acidification of chromium hydroxide filter cake could be separated in a similar manner.

REUSE OF CALCIUM SULFATE AS A FILTER AID

A bench-scale experiment indicated that the calcium sulfate which is generated during the reacidification of lime-precipitated chromium hydroxide filter cake can be reused as an effective filter aid for the separation of Oil and Grease from subsequent reacidified chrome recovery solutions.

Approximately 500 g of wet calcium sulfate filter cake (60% solids) was resuspended in the acidified, recovered chrome solution at a weight ratio of one-to-one. Filtration of the slurry on a vacuum filter leaf at 20 inches of mercury and at room temperature indicated that vacuum filtration is possible at a slurry feed rate of 9.5 gal/ft^2-hr yielding 35 lb/ft^2-hr of dry cake solids (40% moisture) and 5.0 gal/ft^2-hr of filtrate. The Oil and Grease concentration was thus reduced by 90% from a feed concentration of 912 mg/l to 92 mg/l in the filtrate. In contrast to these findings, however, direct filtration of reacidified chrome without "enrichment" with $CaSO_4$ is practically impossible.

SECTION VII

CHROME RECOVERY SYSTEM DESIGN

CAPTURE OF SPENT CHROME

One-bath chrome tanning is the process in which hydrated chromic sulfate complexes react with the biologically-occurring, fibrous protein substrate, collagen, to form leather. One widely-used means of driving this chrome fixation-reaction to practical completion is the offering of an excess of chromium (III) sulfate. In modern practice, as much as 150% of the chrome ultimately taken up by the hide may be offered. The excess chrome is discharged to plant sewers when tanning is complete. Following the discharge of these spent tanning liquors, relatively large volumes of wash waters are used to remove surface impurities and to extract unwanted salts and Oils & Greases from the tanned hides.

As demonstrated in Table 28, for a typical hide processor run approximately 47 pounds of excess chrome (as Cr) is discharged during the initial 800-1,000 gallon spent chrome drain. However, to capture the next 29 pounds of chromium discharged, more than 4,000 gallons of combined drains and washes would have to be collected. An additional four pounds of chromium is "lost" to the floor drains during the unloading of the tanned hides. Thus, as much as 80 pounds of chromium may be discharged in 5,100 gallons of waste from a single hide processor. Even though these tanyard discharges are the major contributors of chromium to the total tannery effluent, sequential, 24-hour wastewater surveys, conducted during the annual plant shutdown, demonstrated that as much as one-third of the chrome comes from non-tanyard activities. For example, a mass-balance blue stock analysis (Section XVI) suggests that approximately 14% of the chromium in the effluent is introduced through blue stock wringing. Likewise, substantial loadings from piling, retanning, coloring, setting, pasting and even "dry-end" operations are suspected. Thus, to maximize chrome capture, essentially all wastewaters generated after tanning (approximately 720,000 gallons/day) would have to be collected for chrome recovery. Clearly, for an urban tannery such a recovery scheme would not optimize valuable space resources. Also, numerous non-chromium components (such as vegetable tannins, buffing dust, Oils & Greases, etc.) would contribute to the formation of a voluminous low-chromium sludge which would not be suitable for chrome recycle. Thus, in the design of Pfister & Vogel's chrome recovery system, collection, storage and treatment hardware were sized for the recovery of chromium-rich tanyard wastes only.

The several alternative levels of chrome capture and recovery considered are depicted in Table 29. Alternative A requires the collection of the most

TABLE 28. DISTRIBUTION OF CHROMIUM IN HIDE PROCESSOR WASTES

Volume, gal	Cumulative Chromium, mg/l	lb
900	6,260	47
1,400	5,060	59
2,050	3,860	66
2,700	3,150	71
4,050	2,250	76
5,100	1,890	80

TABLE 29. ALTERNATIVE LEVELS OF CHROME CAPTURE

Alternative	Volume,gal/day	Chromium mg/l	lb/day
A	14,400	6,260	752
B	22,400	5,060	944
C	32,800	3,860	1,060
D	43,200	3,150	1,140
E	64,800	2,250	1,220
F	81,600	1,890	1,280

concentrated 900 gallons of spent chrome from each of 16 production runs daily. An estimated 14,400 gallons of spent chrome liquor containing 6,260 mg/l of chromium equivalent to 750 lb/day would be processed.

Alternative B would require the collection and treatment of nearly 22,400 gallons of waste including 900 gallons of concentrated spent chrome liquor and the first 500 gallons of wash water from each production run. The chromium concentration would be diluted to 5,060 mg/l while nearly 950 lb of chromium would be removed daily. Likewise, Alternatives C, D, and E call for increased design loadings and corresponding reductions in average chromium concentration. Since substantial quantities of water are required for the practical unloading of tanned hides from hide processor equipment, the final 1,050 gallons from each production run is currently being discharged to floor drains and/or to common plant sewers. Therefore, Alternative F remains hypothetical until a means of collecting this final waste fraction is determined.

At Pfister & Vogel, only 61% of the lower tannery production is done in hide processors with pump out facilities. The remaining 39% of production is conducted in process equipment utilizing gravity discharge of wastes to common tannery sewers. Segregation of this latter portion of the spent chrome liquors is not currently feasible. However, anticipating the possible conversion of these production units to a pump-out design, Alternatives A-F include the capacity to treat chrome-bearing wastes from 16 production runs per day.

PRECIPITATION

The principal objective in spent chrome recovery is the concentration of chrome in relatively dilute process wastes to yield a sufficiently chrome-rich by-product which can be recycled, while substantially reducing effluent levels. As demonstrated during the chrome recovery feasibility studies (Section VI), the most effective means of achieving this chromium separation/concentration is by precipitation with alkali followed by sludge thickening and filtration.

One of the most important factors in the design of an efficient treatment system for chrome recovery is the correct choice of alkali for precipitation. While all of the alkalis investigated (soda ash, aqueous ammonia, hydrated lime and caustic soda) demonstrate excellent chromium hydroxide precipitation capability, hydrated lime was found to be superior.

Chromium hydroxide has a relatively low particle density and it is highly hydrated in an aqueous system. Thickening is impractical within the observed range of suspended solids concentrations without further chemical treatment. Only hydrated lime-chromium hydroxide precipitate responds favorably to the addition of coagulants and/or flocculants to yield large, dense, rapidly settling floc particles. The formation of calcium sulfate during the lime addition is believed to further improve floc density and settling. The lime-precipitated sludge is readily filtered to yield a high-chromium filter cake suitable for land fill or subsequent acidification and reuse.

Soda ash proved to be the least effective precipitating agent during the feasibility studies. The extremely slow settling rate of soda ash-precipitated chromium hydroxide necessitates incorporation of excessive thickener surface area for treating dilute wash waters. The soda ash-precipitated chromium hydroxide sludge, however, is dewatered by vacuum filtration as readily as lime-precipitated sludge. Further, the soda ash sludge produces a substantially thicker filter cake leading to improved cake discharge during vacuum filtration.

Thus, while soda ash must be eliminated where treatment of the most dilute chrome fractions is required, it remains a viable alternative for chrome recovery from concentrated spent chrome liquors viz: Alternatives A and B, where filtration of the unthickened sludge directly after precipitation is favored.

One major disadvantage of the use of hydrated lime over the other alkalis is the formation of large quantities of insoluble calcium sulfate upon acidification with H_2SO_4. The suspended solids remaining after redissolving the lime-precipitated chrome cake equal nearly 15% of the weight of the reclaimed chrome solution. An additional unit operation must be employed to reduce the calcium sulfate content to levels which are tolerable for recycle. Removal of the calcium sulfate can be achieved by hydroclonic separation and/or gravity settling. Ultimate disposal of the resultant calcium sulfate-chrome sludge, however, remains a major drawback to the use of lime.

Where recycle of the chrome is not desired, the lime-precipitated chrome cake can be buried in sanitary landfills. Use of an excess of lime (i.e., more than the stoichiometric requirement) should insure that the trivalent chromium remains "fixed" as the insoluble hydroxide precluding the possibility of leaching through the soil. Finally, on the basis of chemical costs, hydrated lime at $1.25 per pound equivalent ($3.28/100 lb) is substantially cheaper to use as a precipitating agent than is soda ash which costs $5.33 per pound equivalent ($5.01/100 lb).

Therefore, because lime is a superior precipitating agent yielding a chromium hydroxide sludge which settles rapidly and filters readily, and because of its marked cost advantage over other alkalis, the treatment hardware for this project was designed to recover chrome by the lime-precipitation route. Fortuitously, this design also permits the optional precipitation and filtration of the more concentrated chrome wastes by the soda ash route, due to the similar filtration rates for the two types of sludge.

COLLECTION

During normal production scheduling a maximum of two hide processors (out of a total of eleven "on-line" production units with pump-out facilities) discharge chrome wastes within any two hour period. Therefore, screening and collection facilities were sized to handle the simultaneous discharge of wastes from two processing units. For screening, a 48" wide Bauer Hydraseive with 0.040" screen surface openings, having a design loading of 340 gpm was specified. The screened chrome-bearing wastes are discharged by gravity to the 12 ft by 12 ft cylindrical fiberglass Spent Chrome Collection Tank having a capacity of 10,200 gallons.

DESIGN

Sludge Thickening

The sludge thickening tank is among the major hardware items required for chrome recovery. Since space is a limiting factor in this Pfister & Vogel demonstration project (as it is in most urban-located, high productivity tanneries), the comparative space requirements for each of the alternative levels of spent chrome capture and recovery must be known.

Loadings for Alternatives A through F are shown in Table 30. Feed chromium concentrations for the various alternatives vary from 6,260 mg/l to only 1,890 mg/l. Corresponding suspended solids loadings were extrapolated from the suspended solids (lime-precipitated) vs. chromium curve (Figure 7) generated during the feasibility studies. As shown, while suspended solids concentrations are expected to vary from 47,500 mg/l to 9,800 mg/l, the daily solids loading would only vary from 5,700 lb to 6,850 lb.

Design surface areas were determined empirically from the graphical data in Figure 10. Table 31 shows the extrapolated design volumetric loadings which would vary from 400 gpd/ft^2 at a feed suspended solids concentration of 47,500 mg/l to 1,800 gpd/ft^2 at a concentration of 9,800 mg/l. Area requirements calculated from design volumetric loadings and anticipated flow vary from 36.0 ft^2 to 45.3 ft^2, respectively. Corresponding decreases in retention time and underflow concentration as extrapolated from Figures 11 and 12, respectively, are also indicated. Alternatively, surface area requirements can be calculated from extrapolated values of sludge thickener unit areas from Figure 13. Thus, as Table 32 shows, for Alternatives A through E the unit area is a nearly constant 12.1 ft^2/ton-day. For Alternative F, however, because of the unhindered settling characteristics of the low concentration sludge, the unit area is increased to 13.3 ft^2/ton-day. The surface area requirements thus calculated are in very close agreement with the values determined by the design volumetric loading formula.

Filtration

The second major hardware item required for chrome recovery is a filter. A rotary vacuum drum filter was chosen based on its demonstrated effectiveness in dewatering chromium hydroxide sludges. This type of filter lends itself to reliable, automated operation while the capital cost is substantially lower than for a comparable pressure filter.

During the operation of the pilot vacuum filter, a sludge feed rate of 6.6 gal/ft^2-hr was observed with a lime-precipitated chromium hydroxide

TABLE 30. SURFACE AREA FOR SLUDGE THICKENING - PART I

Alternative	Volume, gal/day	Cr mg/l	Cr lb/day	Suspended solids, mg/l	Suspended solids, lb/day
A	14,400	6,260	752	47,500	5,700
B	22,400	5,060	944	35,500	6,630
C	32,800	3,860	1,060	24,900	6,800
D	43,200	3,150	1,140	19,000	6,850
E	64,800	2,250	1,220	12,300	6,650
F	81,600	1,890	1,280	9,800	6,660

TABLE 31. SURFACE AREA FOR SLUDGE THICKENING - PART II

Alternative	Suspended solids, mg/l	Flow, gal/day	Design volumetric loading, gpd/ft^2	Area, ft^2	tu, min	cu, mg/l
A	47,500	14,400	400	36.0	66	84,500
B	35,500	22,400	550	40.8	49	67,500
C	24,900	32,800	800	41.0	35	51,500
D	19,000	43,200	1,050	41.2	27	43,000
E	12,300	64,800	1,500	43.2	18	33,000
F	9,800	81,600	1,800	45.3	14	29,500

TABLE 32. SURFACE AREA FOR SLUDGE THICKENING - PART III

Alternative	Suspended solids, tons/day	Design unit area, ft^2/ton-day	Area, ft^2
A	2.85	12.1	34.5
B	3.32	12.1	40.2
C	3.40	12.1	41.2
D	3.42	12.1	41.4
E	3.32	12.1	40.2
F	3.30	13.3	43.9

containing 38,440 mg/l of suspended solids. Table 20 (Section VI) indicates that the predicted feed rate for a 30,100 mg/l sludge (the minimum sludge concentration anticipated is 29,500 mg/l for Alternative F) at a drum speed of 0.1 rpm is 7.19 gal/ft^2-hr. Even though significant rate increases are projected for higher solids concentrations, the more conservative 6.6 gal/ft^2-hr pilot rate was used to calculate design filter areas for each of the six alternative treatment levels because of our higher level of confidence in the field pilot data.

Anticipated sludge volumes and concentrations for each of the six alternatives are shown in Table 33. Likewise, design filter areas are shown along with expected filter yields. Surface area requirements vary from a minimum 51 ft^2 to handle 8,100 gpd at 84,500 mg/l suspended solids to 171 ft^2 required for 27,100 gpd at 29,500 mg/l.

While the calculated filter area requirements increase proportionately with increases in sludge volume, the cost per square foot of filtering surface for rotary vacuum drum filters decreases substantially within the 50-250 ft^2 range. For example, a major filter supplier's estimated cost for a 110 ft^2 rotary vacuum drum filter (June 1973) equalled \$184/ft^2, while the estimated cost per foot for a 227 ft^2 filter was only two-thirds of that value (\$123/ft^2). This cost effectiveness weighed heavily in the final decision to design the chrome recovery facility for Alternative F levels. However, the determining factor in the design for the treatment of all 81,600 gpd of tanyard chrome-bearing wastes was the observed space efficiency for chromium hydroxide thickening.

TABLE 33. FILTER AREA FOR CHROMIUM HYDROXIDE

Alternative	Settled sludge volume, gpd	Feed solids, mg/l	Feed solids, lb/day	Area, ft^2	Filter yield, lb/ft^2-hr
A	8,100	84,500	5,700	51	4.67
B	11,800	67,500	6,630	75	3.68
C	15,900	51,500	6,800	100	2.83
D	19,100	43,000	6,850	121	2.36
E	24,200	33,000	6,650	153	1.81
F	27,100	29,500	6,600	171	1.62

The theoretical area required for chromium hydroxide thickening as shown in Table 31 is 45.3 gpd/ft^2. Since in full-scale operations settling always deviates from the ideal, a design factor of 1.75 (the normal range of applied factors is 1.0-2.0) has been applied. The area was increased an additional 25% to provide capacity for future production increases. Thus, the calculated area for thickening is:

$$45.3 \text{ ft}^2 \times 1.75 \times 1.25 = 103 \text{ ft}^2$$

A twelve foot diameter, 90° conical bottom fiberglass tank, having a nominal surface area of 113 ft^2 and a 5 ft sidewall (overall depth 11 ft), was chosen. After installation of the flocculation-distribution chamber, the actual area available for thickening was reduced to 107 ft^2.

As shown in Table 33, 171 ft^2 of filter area is required to handle the 27,100 gallons of sludge to be generated daily. This area was increased by 25% to 214 ft^2, anticipating eventual increases in production levels. A 6' diameter x 12' wide rotary vacuum drum filter with string discharge and a Nylon multi-filament filter cloth was selected. A vacuum of 22" is supplied by a manufacturer-recommended 40 h.p. blower with a nameplate capacity of 600 cfm. Likewise, a self-priming centrifugal pump, rated at 70 gpm, was chosen for filtrate removal. All wetted metal parts were ordered in 316 stainless steel because of the highly corrosive conditions.

Alkali Addition

Equalized spent chrome wastes can be pumped to the Alkali Addition Tank or recirculated to the Spent Chrome Collection Tank with a centrifugal pump. Any desired flow within the 0-80 gpm capacity range can be delivered for precipitation, using an in-line flow meter for control by precise adjustment of the recirculating valve.

An alkali make-up tank has been sized for one 8-hour shift operation of the Chrome Recovery System. A dish-bottom fiberglass tank with an effective capacity of 340 gallons will supply 835 lb of $Ca(OH)_2$ per shift as a 2.5 lb/gallon slurry. The lime slurry is pumped to the Alkali Addition Tank for chromium hydroxide precipitation. Feed rates varying from 0.4 to 5.0 gpm using a progressing cavity positive displacement pump with a variable speed drive are possible. After calibrating the drive setting for the output from the pump, alkali can be delivered proportionally by adjusting the pump drive to the setting required by any given waste acidity.

To insure maximum precipitation of the chromium hydroxide, the Alkali Addition Tank was specified at 400 gallons capacity providing a minimum of 5 minutes retention. A 0.75 hp chemical mixer further insures optimum precipitation. The bottom-center outlet is piped upward to the settling tank feed trough providing a head-leveling device. Thus, during steady state operation, precipitated chrome is withdrawn from the bottom by gravity, while the volume in the Alkali Addition Tank is maintained near the 400 gallon mark.

Flocculation

The precipitated chromium hydroxide is flocculated with a liquid polyelectrolyte - Nalcolyte 677 at a 30 ppm dosage. Polymer solution must be prepared daily in the 100 gallon Polymer make-up tank. A 0.75 hp chemical mixer provides rapid solution of the polymer. A variable discharge 600 ml/min capacity diaphragm pump delivers the high viscosity polymer solution to the head of the settling tank feed trough in proportion to wastewater flow. The inclined trough is baffled to effect a "flash mixing" of the polymer with the chromium hydroxide as it is fed to the center of the sludge thickening

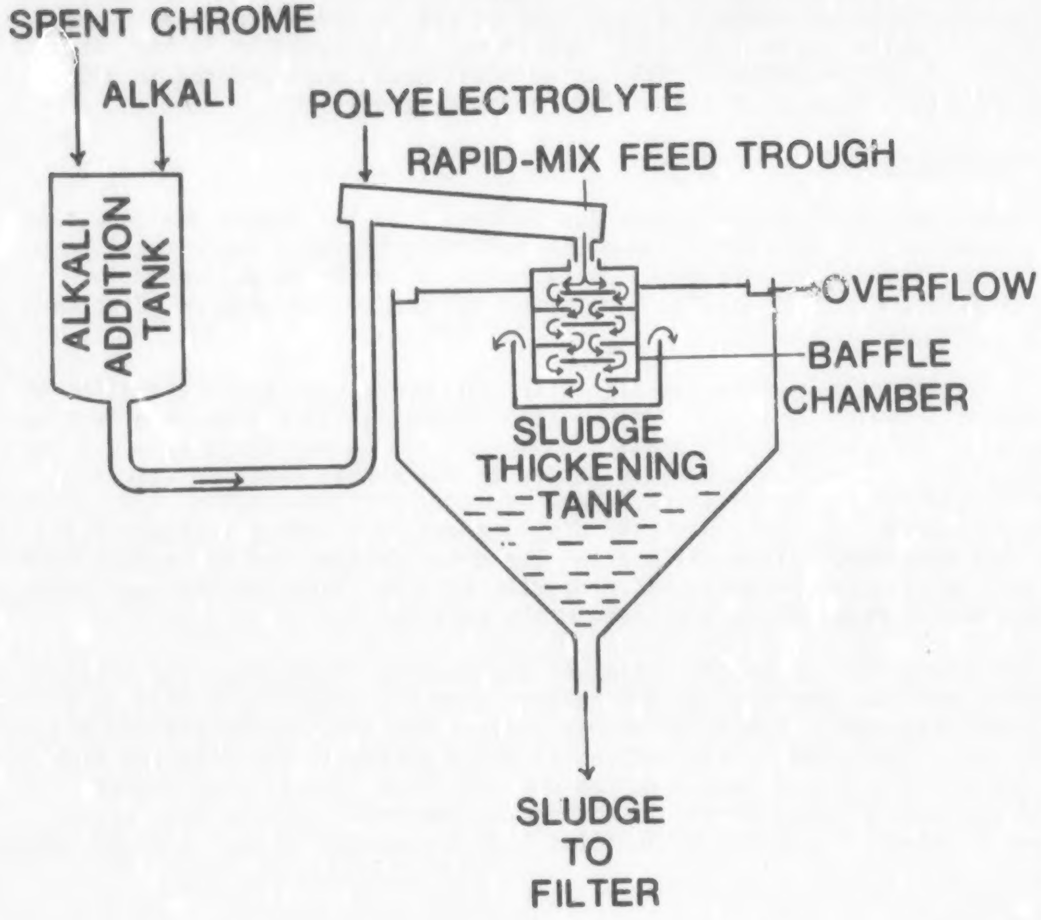
SPENT CHROME
ALKALI
POLYELECTROLYTE
RAPID-MIX FEED TROUGH
ALKALI ADDITION TANK
OVERFLOW
BAFFLE CHAMBER
SLUDGE THICKENING TANK
SLUDGE TO FILTER

Figure 19: FLOCCULATION OF CHROMIUM HYDROXIDE.

tank. The chromium hydroxide-polyelectrolyte mixture flows into the sludge thickener through the baffle chamber/distribution box, as depicted schematically in Figure 19. A series of parallel plates alternates flow between the center and the perimeter of the central chamber, as illustrated, to effect a gentle mixing pattern conducive to good floc formation. As the sludge leaves the central chamber it is redirected towards the surface by an outer chamber and is ultimately released into the quiescent zone approximately one foot below the surface for settling.

Sludge Pumping

Anticipated operation of the chromium hydroxide sludge thickener will generate sludge at widely varying concentrations. A progressing cavity positive displacement pump was therefore chosen for sludge drawoff because of its nearly constant output per revolution over a wide range of total discharge heads. Also, this type of pump minimizes break-up of the floc particles, therefore improving filtration. A variable speed drive allows operation of the sludge pump anywhere within a 4.0 to 45 gpm range.

Cake Acidification

Chromium hydroxide filter cake from the rotary vacuum drum filter is discharged to a 1000 gallon capacity Cake Solution Tank containing a solution of concentrated sulfuric acid and dissolved filter cake. A 1.5 hp chemical mixer accelerates resolution of the cake, and a compression load cell under the tank allows accurate process control throughout the 0 to 10,000 lb net weight range. During continuous operation of the vacuum filter, chromium hydroxide cake is redissolved to yield 4,000 lb batches of recovered chrome. When the pre-set gross weight of 6000 lbs is reached in the Cake Solution Tank, the feed screw conveyor is shut off and the tank is drained to the 2000 lb level (under design loadings the screw conveyor is sized to hold cake equivalent to one hour's filter operation). The recovered chrome is pumped to a pair of hydrocyclonic separators rated at 22 gpm through-put each at a feed pressure of 50-60 psi. Calcium sulfate sludge is collected in barrels for daily disposal, while the clarified chrome is repumped to a 2,800 gallon capacity fiberglass storage tank. A minimum of 2,000 lbs of dissolved cake is retained in the Cake Solution Tank as a diluent for subsequent feeds of concentrated sulfuric acid. A new batch commences with the addition of the acid (400-500 lb/batch) followed by addition of fresh chromium hydroxide cake.

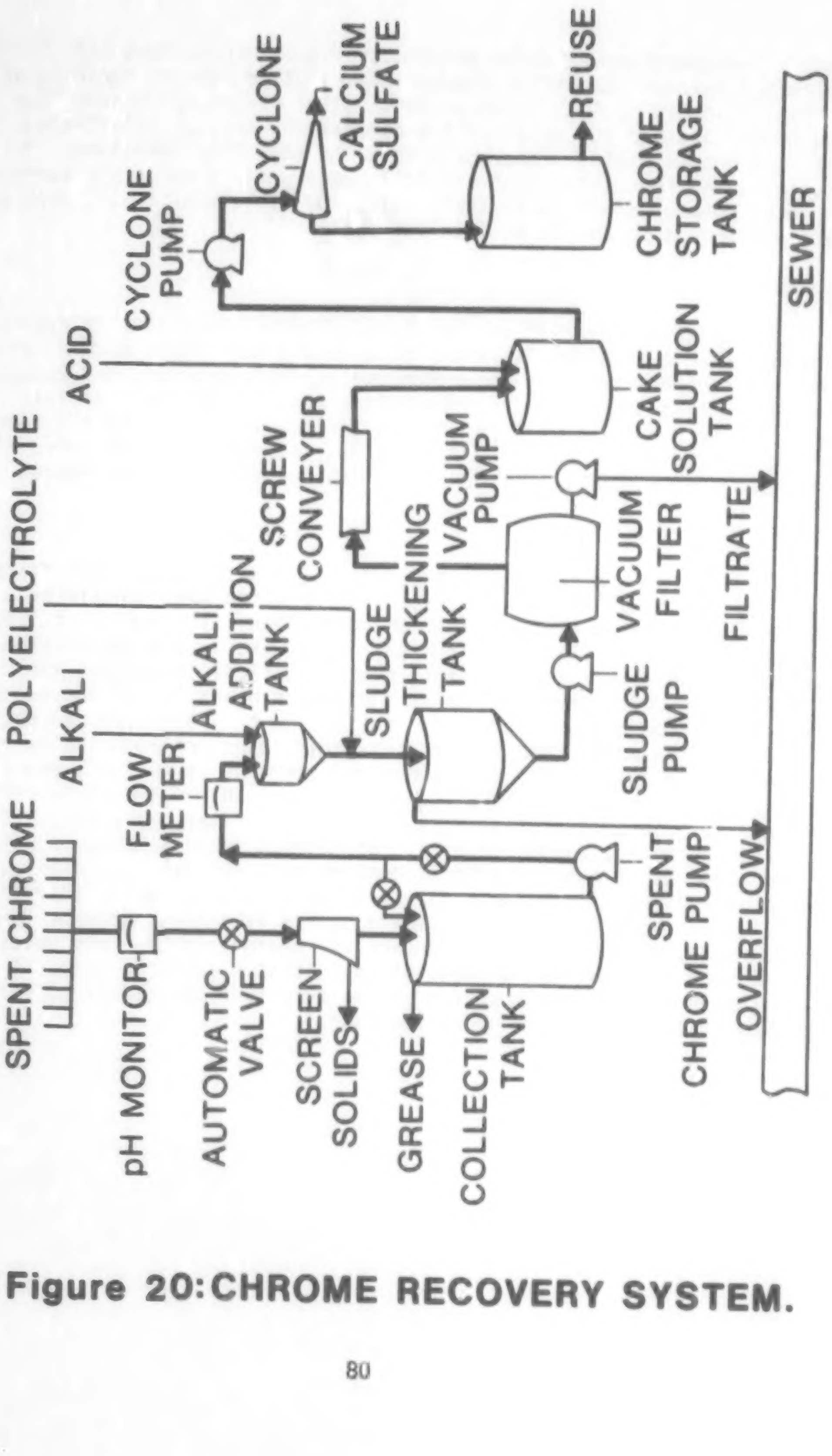
SPENT CHROME
pH MONITOR
AUTOMATIC VALVE
SCREEN
SOLIDS
GREASE
COLLECTION TANK
SPENT CHROME PUMP
OVERFLOW
FLOW METER
ALKALI
POLYELECTROLYTE
ALKALI ADDITION TANK
SLUDGE THICKENING TANK
SLUDGE PUMP
SCREW CONVEYER
VACUUM PUMP
VACUUM FILTER
FILTRATE
ACID
CAKE SOLUTION TANK
CYCLONE PUMP
CYCLONE
CALCIUM SULFATE
REUSE
CHROME STORAGE TANK
SEWER

Figure 20: CHROME RECOVERY SYSTEM.

SECTION VIII

CHROME RECOVERY SYSTEM--FULL SCALE OPERATION

The full-scale Chrome Recovery System, as illustrated in Figure 20, incorporates collection, storage, precipitation, sludge thickening, filtration and cake dissolving facilities for all tanyard chrome-bearing wastes, all within a 1000 ft^2 plant area.

Chrome-bearing wastes are pumped from each processing unit through a common collection "header" pipe to a gravity screen (0.040" openings). The pH in the chrome header is monitored continuously to protect against a catastrophic introduction of sulfide bearing wastes into the Chrome Recovery System. If the pH rises above the alarm level, an automatic air solenoid-operated valve closes and a horn alerts operating personnel to the upset.

The screened spent chrome solution is discharged to a 10,200 gallon capacity collection-equalization-flotation tank, while the relatively small amounts of suspended solids are collected for regular disposal. In the Spent Chrome Collection Tank, Oils and Greases separate from solution by gravity to form a surface-scum layer which can be skimmed (or siphoned) off daily for disposal. The low Oil and Grease underflow from the collection tank is metered to the Alkali Addition Tank and mixed with a proportioned feed of alkali. The chromium hydroxide suspension overflows the Alkali Addition Tank into a "rapid-mixing" trough feeding the conical-bottom Sludge Thickening Tank. Polyelectrolyte is added at the head of the mixing-trough. The inlet to the thickener consists of a sub-surface baffle chamber which induces floc formation and distributes the waste radially into the settling zone. Flocculated chromium hydroxide settles into the conical sludge thickening zone, while clarified effluent overflows a weir at the tank surface. A positive displacement pump conveys the thickened sludge to the slurry tank of a rotary vacuum drum filter. Filtrate from the vacuum filter can be sewered, or, if necessary, may be recycled to the Alkali Addition Tank to utilize any available alkali and improve chrome removal. The filter cake is removed by a string discharge mechanism, dumped onto a screw conveyor and transported to the cake solution tank where it is dissolved in concentrated sulfuric acid. The recovered chrome solution is pumped under pressures of 50-60 psi to a hydrocyclonic separator to remove suspended calcium sulfate. The calcium sulfate sludge, thus generated, is discharged into a hopper for subsequent treatment and/or disposal. The "overflow" from the cyclones is pumped to the recovered chrome storage tank for reuse in the tanning process.

Full-scale, 8-hour continuous operation of the Chrome Recovery System confirms the design data developed during the bench- and pilot-scale investigations.

At a capture level of approximately 500 lbs of chromium per day, treatment efficiencies in excess of 98%* removal were recorded. Recovered, acidified chrome liquor containing 0.6 lb Cr_2O_3/gal was produced at the rate of 1,000 to 1,200 gallons per day. Concomitantly, 3,000 to 3,600 lb of suspended solids as well as 330 lb to 585 lb of Oil and Grease were also removed.

Lime-precipitation of the most concentrated spent chrome liquors, discharged during one 24-hour period, yielded approximately 10,000 gal of chromium hydroxide suspension. Observed solids loadings to the sludge thickening unit slightly exceeded the 164 lb/ft^2-hr design loading. Likewise, volumetric loadings of 516 gpd/ft^2 exceeded the design rate of 400 gpd/ft^2 for concentrated chrome. The sludge, thus generated, contained 7% solids, and was dewatered to yield a cake of 30-35% solids. Incremental rates for the filtration of lime-precipitated chromium hydroxide as high as 7.5 gal sludge/ft^2-hr were observed (design rate=6.6 gal/ft^2-hr) with corresponding filter yields in excess of 3.7 lb dry solids/ft^2-hr. Even though these optimal operation rates for the Chrome Recovery System cannot be maintained for the total 8 hour interval, average filter rates as high as 5.1 gal/ft^2-hr with a corresponding yield of 3.0 lb dry solids/ft^2-hr have been observed. Further, removal of Oil and Grease as a 50% scum effected a 92-95% reduction through the use of the underflow draw-off from the Spent Chrome Collection operation. Less than one percent of the Oil and Grease was discharged to the sewer as filtrate and settling tank overflow, while the remainder concentrated in the filter cake and was thus recycled.

Solids which require daily disposal include approximately 2,000 lb of chrome contaminated calcium sulfate sludge, as well as about 150 gallons of supernatant Oil and Grease "scum". Also, about 3 gallons of screenings are collected which may be reduced to three pounds of screened solids by a second pass over the static screen.

CHROME RECOVERY BY LIME PRECIPITATION

In another 8-hour continuous chrome recovery run, 9600 gallons of concentrated spent chrome liquor was collected from eleven hide processors over a 24 hour period. The spent chrome, which contained 6,320 mg/l of chromium (506 lb Cr), was precipitated by the addition of 1,050 lb of hydrated lime (as a 2.5 lb $Ca(OH)_2$/gal slurry) within 4.5 hours to generate 10,000 gal of chromium hydroxide suspension. As shown in Table 34, the resultant suspended solids concentration equalled 38,420 mg/l. Approximately 120% of the stoichiometric dosage of lime was required to maintain pH within the 8.7 to 9.0 range. After the controlled addition of 30 ppm of liquid polymer (Nalcolyte 677 added as a 1% solution), the chromium hydroxide sludge was fed at a rate of 38.5 gpm to the sludge thickener which was pre-charged with 6,000 gal of supernatant from a prior run. The equivalent volumetric loading was thus 516 gpd/ft^2 (107 ft^2 surface area), while the solids feed rate averaged 166 lb/ft^2-day.

* Since "end-of-the-pipe" chromium levels of 1340 lb Cr per day are typical overall effluent reductions of approximately 37% are calculated.

TABLE 34. CHROME RECOVERY SYSTEM PERFORMANCE - LIME PRECIPITATION - PART I

	Volume, gallons	TSS,		TS,		Cr,	
		mg/l	lb	mg/l	lb	mg/l	lb
Spent Chrome	9,600	-	-	-	-	6,320	506
Feed	10,000	38,420	3,200	101,480	8,460	6,040	503
Overflow	4,850 *	1,740	70.3	68,480	2,760	250	10.1
Sludge	5,150	72,060	3,090	126,460	5,430	11,120	478
Filtrate	4,300 **	82	39.4	61,440	1,810	3.4	0.12
Cake	(9,960 lb)	-	-	(30.25%)	3,020	-	-
Cyclone Feed	1,155	205,000	1,970	-	-	-	-
Recovered Chrome	1,010	79,200	666	300,416	2,530	53,800	452
$CaSO_4$	145 (2,020 lb)			(58.8%)	1,190	(2.22%)	44.9

* By difference

** Estimated at 83% of sludge volume, per feasibility studies.

Throughout the course of the 4.5 hour thickening operation, severe foaming was observed. A thick pillow of foam was also observed above the Alkali Addition Tank and the sludge thickener feed trough suggesting that foaming was a consequence of the lime addition and mixing (turning off the high speed chemical mixer, however, did not significantly reduce foaming). This foaming adversely affected the separation process as 1,740 mg/l of suspended solids and 250 mg/l of chromium were detected in the settling tank overflow. Also, a sample of collapsed foam from the settling tank analyzed at 9,570 mg/l of chromium. As a result of this foaming, 2.2% of the suspended solids and 2.0% of the chromium contained in the sludge feed was discharged in the overflow. This problem of foaming was subsequently corrected by re-design of the Alkali Addition Tank overflow-head leveling device and the feed trough to decrease the velocity of the feed to the sludge thickener.

Withdrawal of freshly thickened sludge commenced two hours after the chromium hydroxide feed began. Approximately 5,200 gal of sludge at a mean suspended solids concentration of 72,060 mg/l was drawn off at an average rate of 15 gpm and filtered on the rotary vacuum drum filter in 5.67 hours. Cake thickness ranged from 4.8mm to 6.4mm. At a drum speed of 0.115 rpm, 37.5% maximum submergence and under a cake form vacuum of 26" of mercury, an average sludge feed rate of 4.1 gal/ft^2-hr to the filter was maintained. This corresponds to an average filter yield of 1,750 lb of wet cake per hour at approximately 30% solids-equivalent to 2.34 lb dry solids/ft^2-hr. During the final hour of filter operation a maximum filter rate of 6.6 gal feed/ft^2-hr was observed with a corresponding filter yield of 2.86 lb dry solids/ft^2-hr.

Approximately 4,300 gallons of filtrate containing only 82 mg/l of suspended solids and 3.4 mg/l of total chromium was also produced.

Acidification of the filter cake required 1,500 lb of sulfuric acid (66° Be′) and yielded 1,155 gallons of a recovered chrome-calcium sulfate suspension containing 205,000 mg/l of suspended solids (of which 153,000 mg/l were fixed suspended solids). This slurry was fed at an average rate of 33.5 gpm to a pair of hydrocyclonic separators with orifice diameters of 3/16" (Bauer Clarifier No. 677-1). Approximately 200 gallons of sludge was generated and subsequently decanted to produce 145 gallons (0.72 yds) of thickened calcium sulfate containing 58.8% solids (57% fixed solids) and 2.22% Cr. The "overflow" from the cyclones plus the decanted supernatant from calcium sulfate sludge thickening equalled 1,010 gallons and contained 80,500 mg/l of suspended solids for a 61% reduction. The recovered chrome analyzed at 0.655 lb Cr_2O_3/gal (0.448 lb Cr/gal), with a pH of 2.9 and a basicity of 39.4%.

As Table 34 illustrates, of the 506 lb of chromium charged to the Chrome Recovery System, 10.1 lb was discharged as overflow, and another 0.12 lb was discharged as filtrate, for a net removal efficiency of 97.98%. A substantial 8.86% of the chromium (44.9 lb Cr) was transferred to the calcium sulfate sludge, which would ultimately require land disposal. Likewise, of the 3,200 lb of suspended solids entering the sludge thickener, 70.3 lb was found in the overflow and 39.4 lb in the filtrate, for a net removal of 96.58%.

TABLE 35. CHROME RECOVERY SYSTEM PERFORMANCE - LIME PRECIPITATION - PART II

	Volume, gallons	Suspended solids,		Total solids,		Total fixed solids,		Oil & Grease		Cr	
		mg/l	lb	mg/l	lb	mg/l	lb	mg/l	lb	mg/l	lb
Spent Chrome	9,940	-	-	-	-	-	-	7,460	618	6,000	497
Feed	10,300	42,060	3,620	105,200	9,050	100,160	8,720	379	32.5	5,820	500
Overflow	4,160*	300	10.4	72,180	2,490	71,108	2,460	39	1.35	10.3	0.36
Sludge	6,140	67,740	3,460	125,680	6,440	115,980	5,930	671	34.3	9,340	478
Filtrate	5,100**	210	8.9	73,380	3,140	72,260	3,070	18	0.76	2.10	0.09
Cake	(10,800 lb)	-	-	(33.4%)	3,610	(26.72%)	2,880	(0.31%)	33.7*	-	-
Cyclone Feed	1,185	252,800	2,500	566,260	5,480	308,260	2,790	-	-	48,500	480
Recovered Chrome	1,035	154,000	1,330	464,960	4,010	246,280	2,130	-	-	49,200	426
$CaSO_4$	(1,850 lb)	(58.2%)	1,080	-	-	(44.0%)	814	-	-	(2.65%)	49

* by difference

** estimated at 83% of sludge volume, per feasibility studies

In another typical chrome recovery run 9,940 gallons of concentrated chrome liquor from eleven hide processors, containing 497 pounds of total chromium (6,000 mg/l), was processed within an 8-hour production shift. As shown in Table 35, 1,035 gallons of 25% basicity recovered chrome (at 0.60 lb Cr_2O_3 per gallon) and 1,850 lb of calcium sulfate sludge were generated. Elimination of foaming during lime-precipitation of the chromium hydroxide greatly improved the chrome separation efficiency to 99.9%, yielding average supernatant and filtrate chromium concentrations of only 10.3 mg/l and 2.10 mg/l, respectively.

The spent chrome was precipitated with 1,200 lb of hydrated lime (as a 4.0 lb/gal slurry) and flocculated with 30 ppm of Nalcolyte 677 polyelectrolyte, to generate 10,300 gallons of chromium hydroxide suspension. The slurry was fed to the sludge thickener at a mean suspended solids concentration of 42,060 mg/l within a 6 hour interval. Accordingly, an average volumetric loading to the sludge thickening unit of 375 gpd/ft^2 was demonstrated with a corresponding solids feed rate of 135 lb dry solids/ft^2-day.

An Oil and Grease reduction of 94.7% was effected through gravity separation in the Spent Chrome Collection Tank. While the raw waste analyzed at 7,460 mg/l of Oil and Grease (618 lb), the feed to the sludge thickening unit contained only 379 mg/l. The Oil and Grease-laden scum was manually skimmed from the Spent Chrome Collection Tank through an overflow, and collected for eventual land disposal.

Of the Oil and Grease remaining after gravity separation, an estimated 33.7 lb was concentrated in the filter cake, while the sludge thickener overflow and the filtrate contained only 1.35 lb and 0.76 lb, or 0.22% and 0.12%, respectively.

An estimated 4,160 gallons of overflow were generated, containing 300 mg/l of suspended solids and only 39 mg/l and 10.3 mg/l of Oil and Grease and chromium, respectively.

Approximately 90 minutes after the initial precipitation of chromium hydroxide, the withdrawal of thickened sludge for vacuum filtration commenced at an average rate of 19.3 gpm. Within 5.33 hours, 6,140 gallons of thickened sludge containing 67,740 mg/l of suspended solids was filtered at an average feed rate of 5.1 gal/ft^2-hr. The corresponding filter yield was 2,040 lb wet cake/hour (33.4% solids) equivalent to 2.99 lb dry solids/ft^2-hr. The maximum incremental feed rate to the filter was 7.5 gal/ft^2-hr, while a maximum incremental filter yield of 3.93 lb dry solids/ft^2-hr was realized.

The filter cake, which averaged 33.4% solids, was dissolved in 1,350 lb of sulfuric acid to yield 1,185 gallons of chrome-calcium sulfate slurry, containing 252,800 mg/l of suspended solids. Hydrocyclonic separation of this slurry effected a 39% reduction in suspended solids to yield 1,035 gallons of recovered chrome and 150 gallons of a 58.2% calcium sulfate solids sludge.

A mass-balance analysis (Table 35) of this chrome recovery run reveals that while a total of only 0.45 lb of chromium was discharged in the sludge thickener overflow and filtrate, an additional 49 lb or 10.2% of the chromium contained in the cyclone feed was discharged with the calcium sulfate sludge, requiring land disposal. Thus, the recovery efficiency for this run was actually only 86%, with 426 lb Cr in the recovered chrome and an estimated 19 lb Cr was retained in the sludge thickener for recovery in the subsequent run.

CHROME RECOVERY BY SODA ASH PRECIPITATION

To eliminate the calcium sulfate separation and disposal required for chrome recovery by the lime precipitation process, soda ash was substituted. The operating procedures which were eventually adopted differed from those required for lime due to the extremely slow settling rate of soda ash-precipitated chromium hydroxide. The most concentrated spent chrome liquors from eleven hide processors could be precipitated and charged to the sludge thickening unit within a single 8-hour shift. Only about 70% of the equivalent quantity of chromium hydroxide filter cake, however, could be generated within the same interval. After allowing precipitated sludge to thicken overnight, approximately 11,000 gallons of fresh chromium hydroxide was charged to the sludge thickener on the following day, while a proportional quantity of day-old thickened sludge was simultaneously drawn off and filtered within eight hours.

In one run, 9,100 gallons of spent chrome was precipitated with soda ash and the freshly thickened sludge was simultaneously withdrawn for filtration within the same 8-hour interval. Chromium hydroxide suspension containing 24,000 mg/l of suspended solids was fed to the sludge thickening unit over a 7-hour period at an average rate of 24.2 gpm. The average volumetric feed rate to the sludge thickener was 329 gpd/ft^2, while a corresponding solids feed rate of 66 lb dry solids/ft^2-day was observed.

The fact that a small amount of aged sludge from the previous chrome recovery run remained in the sludge thickener is illustrated by the observed 98,000-99,000 mg/l sludge concentrations during the first hour of sludge withdrawal. After two hours, however, sludge suspended solids leveled off and remained nearly constant throughout the final six hours of sludge withdrawal.

Filtration of 7,000 gallons of sludge, which averaged 35,000 mg/l of suspended solids, yielded 7,500 lb of filter cake within eight hours. The average rate of thickened sludge feed during 7.67 hours of vacuum filtration was 4.0 gal/ft^2- hr (912 gal/hr), while filter yield averaged 980 lb wet cake per hour, equivalent to 1.12 lb dry solids/ft^2-hr.

Acidification of the filter cake required 950 lb of 66° Be' sulfuric acid and yielded 850 gallons of recovered chrome liquor, which analyzed at 0.596 lb Cr_2O_3/gal (0.408 lb Cr/gal) and 33.7% basicity.

In another soda ash-precipitation run, day-old thickened sludge was withdrawn from the sludge thickener and filtered, while 9,700 gallons of fresh spent chrome was simultaneously charged to the Chrome Recovery System, increasing the yield of recovered chrome within an 8-hour production shift to 1,200 gallons containing 742 lb of Cr_2O_3 (508 lb Cr).

The spent chrome which was collected from eleven hide processor runs (four of which were completed during the 8-hour chrome recovery run) contained 6,170 mg/l of Cr and required the stoichiometric addition of 2,350 lb of Na_2CO_3 (as a 2 lb/gal solution) to yield 10,850 gallons of chromium hydroxide precipitate at a pH of 8.5-9.0. The chromium hydroxide slurry was charged to the sludge thickener at the average rate of 22.6 gpm, equivalent to a volumetric loading of 305 gpd/ft^2. A solids feed rate of 62.5 lb/ft^2-day was observed at a mean feed suspended solids concentration of 24,700 mg/l.

As shown in Table 36, the overflow generated equalled half of the feed volume and contained 710 mg/l of suspended solids, equivalent to 1.5% of the feed solids. Chromium and Oil and Grease in the overflow were likewise reduced to 169.5 mg/l and 57 mg/l, respectively.

Approximately 5,400 gallons of sludge was withdrawn over the eight hour run, averaging 49,000 mg/l of suspended solids. Filtration of the sludge yielded 10,600 lb of cake which contained 4.85% Cr and 76.4% H_2O. The mean rate of filtration was 3.0 gallons of feed per ft^2-hr while the filter yield averaged 1.21 lb dry solids/ft^2-hr (1,160 lb wet cake/hr) and cake thickness ranged from 4.0mm to 8.0mm. The maximum incremental filter rate observed was 4.5 gal feed/ft^2-hr and incremental filter yields exceeded 1,980 lb wet cake/hr equivalent to 2.05 lb dry solids/ft^2-hr.

Reacidification of the cake required 1,350 lb of H_2SO_4 and yielded 1,200 gallons of recovered chrome liquor at a pH of 3.2 containing 0.618 lb Cr_2O_3/gal (0.42 lb Cr/gal).

Approximately 4,300 gallons of filtrate were generated containing 302 mg/l (10.8 lb) of suspended solids. Thus, only 0.5% of the feed solids charged to the sludge thickener was discharged as filtrate. Likewise, Oil and Grease analyzed at 30 mg/l and chromium at 40.5 mg/l.

As Table 36 illustrates, the 9,700 gallons of spent chrome collected from eleven hide processors contained 498 lb of chromium. The chromium thus captured comprises approximately 37% of Pfister & Vogel's "end-of-the-pipe" effluent chrome loading. A mass-balance analysis of our chrome recovery operation using soda ash to precipitate the chrome shows that 98.1% recovery of the isolated chromium has been achieved. The sludge thickener overflow contained 1.6%, while the filtrate contained only 0.3% of the chromium input to the Chrome Recovery System. The combined effluent from the settling tank overflow and vacuum filter filtrate equalled 9,775 gallons at an average chromium concentration of 118 mg/l. Likewise, a 98.9% reduction in Oils and Greases sewered during this dynamic collection-recovery process has been demonstrated. Approximately 92% of the Oils and Greases was separated as scum in the Spent Chrome Collection Tank, while only 0.8% and 0.3% were

TABLE 36. CHROME RECOVERY SYSTEM PERFORMANCE - SODA ASH PRECIPITATION

	Volume, gallons	TSS,		TS,		TFS,		Cr,		O&G,	
		mg/l	lb	mg/l	lb	mg/l	lb	mg/l	lb	mg/l	lb
Spent Chrome	9,690	3,800	307	103,190	8,330	81,610	6,580	6,168	498	4,408	357
Feed	10,850	24,700	2,230	107,050	9,780	100,140	9,060	5,495	496	311	28.1
Overflow	5,425	710	32	81,520	3,680	78,000	3,530	179.5	8.12	57	2.58
Sludge	5,425	48,820	2,200	120,520	5,450	107,580	4,870	10,620	481	732	33.1
Filtrate	4,350	302	10.9	85,480	3,230	82,750	3,000	40.5	1.47	30	1.09
Cake	(10,590 lb)	(23.6%)	2,500	(23.6%)	2,500	(17.3%)	1,820	(4.85%)	514	(0.32%)	34.0
Recovered Chrome	1,200	14,500	145	274,000	2,740	199,500	1,995	50,800	508	-	-

found in the thickener-overflow and vacuum filter filtrate, respectively. The remaining Oil and Grease was retained in the filter cake and appeared in the recovered chrome. Also, a 98.2% recovery of suspended solids as filter cake from the chromium hydroxide precipitate has been demonstrated. The combined sludge thickener overflow and vacuum filter filtrate contained an average of 538 mg/l of suspended solids.

CHROME RECOVERY OPERATING COSTS

The costs for recovering the chrome from approximately 10,000 gpd of the most concentrated spent chrome liquors (containing 6,260 mg/l of Cr) has been calculated (Table 37). At January 1976 prices for chemicals, solids disposal, electricity and labor, the cost of recovery by the soda-ash precipitation process is $248.30 per day. The corresponding cost for lime-precipitation is $155.50 per day. Thus, within the price range for commercially available prepared chrome tanning solutions, the estimated net annual savings would vary from $50,000-$126,000 for soda ash to $68,000-$135,000 for lime precipitation.

TABLE 37. CHROME RECOVERY SYSTEM OPERATING COSTS - SODA ASH VS LIME PRECIPITATION

	Unit Cost	Daily Cost,* $ Soda ash	Daily Cost,* $ Lime
Lime	$3.28/100 lb	-	39.40
Soda ash	$5.01/100 lb	117.80	-
Sulfuric acid	$2.58/100 lb	34.80	34.80
Polyelectrolyte	$1.12/lb	-	2.90
CHEMICALS SUB-TOTAL		$152.60	$ 76.10
Electricity	2.2¢/kwh	11.70	8.80
Solids disposal	$3.50/yd^3	-	2.60
Labor	$8.00/hr	64.00	48.00
Sub-Total		228.30	135.50
Contingencies		20.00	20.00
TOTAL		$248.30	$155.50

* Spent chrome volume = 10,000 gpd.

* Spent chrome concentration = 6,260 mg/l as Cr.

RECOVERY OF OILS AND GREASES

Approximately 10,000 gallons of spent chrome was passed through the 48" wide static screen (0.040" openings) and collected in the Spent Chrome Collection Tank. The Oil and Grease was allowed to separate overnight under quiescent conditions. After 16 hours a water hose was inserted midway down the tank and clean water was carefully added to raise the level of the Oil and Grease layer to that of the tank overflow pipe. Approximately 50 gallons of the surface scum (Sp.Gr.=0.945) was skimmed through the overflow and collected. A two-step chloroform extraction of a portion of this scum (pH 3.5) revealed an Oil and Grease content of 51.4%.

Laboratory tests to explore possible routes to purification and/or recovery of the contained Oils and Greases were undertaken as follows:

An aliquot of the scum was allowed to separate under quiescent conditions for two hours. A three-phase separation was observed in which the lower aqueous layer equalled 17% of the original volume. The middle layer which consisted of an oily suspension of tiny fibrous particles equalled 82% of the original volume and the top layer which appeared as a brown semi-translucent oil represented only 1% of the total volume.

Acidification to a pH of approximately 1 effected a two-phase separation with a well defined interface within 2 hours. After 10 minutes boiling on a hotplate and subsequent overnight settling, a three-phase system was established in which the third phase consisted of a top layer of a brown oil.

Another 200 ml aliquot was brought to a boil and allowed to cool and settle overnight. The resultant three-phase separation gave approximately 20% of the oily substance.

Finally, a 7.5 liter portion of the scum was acidified to pH 0.7 with a 5% sulfuric acid solution. Live steam was injected to bring the mixture to a boil for 15 minutes. Overnight settling and cooling to room temperature effected a separation into three phases. Decantation yielded two liters of the brown oily substance. Likewise, another liter of the brown oily suspension which had composed the intermediate layer was segregated.

The brown oil which was separated had a specific gravity of 0.900 and was not steam distillable at pH 1.0. While several materials were investigated to decolorize the oil, including activated charcoal, distilled water, saturated sodium chloride solution, Hyflo Supercel (a filter aid), Celatom (a diatomaceous earth), Clay R and two anionic and one cationic polyelectrolyte solutions, none of these produced a significant decolorization of the oil.

SECTION IX

CHROME RECYCLE - MATCHED PAIRS LEATHER TESTS

Any optimum procedure to be used for the recycle of chrome in the manufacture of leather must be considered first for its "fit" with highly subjective tanning methods and procedures employed by each tanner. At Pfister & Vogel, without seriously disrupting existing processes or equipment utilization, the following routes for chrome recycle could be postulated, and were investigated with varying degrees of success.

REUSE OF SPENT CHROME AS PICKLE FLOAT

A matched-sides, leather-comparative test demonstrated the effect of reusing spent chrome liquor as the pickle float in a subsequent hide processor run. Approximately 850 gallons of spent chrome (equivalent to 50% float) containing 6,390 mg/l of Cr was added to drained bated stock, replacing the normal salt brine feed.

Analysis of the test pickle exhaust liquor revealed that 54% of the chromium was "scrubbed" from the float during the pickle run. Even though 30% excess acid is offered in the recycled liquor, a pickle pH of 3.2 was observed, rather than the "expected" 2.85 for the regular. Approximately two-thirds of this spent pickle liquor (containing 14.3 lb Cr) was sewered, while the remaining 6.5 lb Cr was carried over into the tanning run.

Though the amount of fresh chrome offered in tanning was reduced in the test run by 5%, the chrome exhaust liquor contained 23% more chromium than the regular.

This "one-time" recycle effected a 9% reduction in the total amount of chromium sewered from 75.4 lb Cr for the regular run to an average of 68.7 lb Cr for the two consecutive runs required to demonstrate one reuse of the spent chrome.

Chemical analysis of the finished leather showed only slight differences, with the test sides containing 6.5% more Cr_2O_3 on a hide substance basis.

Analysis of the blue stock after wringing, however, revealed a 14% increase in the Cr_2O_3 content of the test side grains and a 16% increase for the test splits on a moisture free basis, suggesting that further significant reductions in the amount of fresh chrome offered for tanning may be possible. In addition, though there was no measurable difference in the fat content of the grain layers, the splits showed a 33% reduction in fats on a moisture free basis.

At the final sort the test sides were decidedly better for break (eight out of eight), slightly firmer, slightly poorer for flesh and comparable to the regular sides for smoothness, fat wrinkles, surface break, hair cell and veins. The test sides were also consistently lighter in weight than the regulars. Most notably, however, the physical strength of the test sides was substantially poorer, as measured by the Satra grain crack, Satra extension and slot tear. The Satra force was reduced in this test from an average value of 63.8 kg for the controls to 54.6 kg for the test sides, with a corresponding reduction in the extension-at-grain burst from 9.49 mm to 9.04 mm. Likewise, a reduction in slot tear strength from 67 lb to 57 lb was observed.

REUSE OF RECOVERED CHROME BY BLENDING WITH STOCK CHROME

A matched sides leather test in hide processors has demonstrated the leather quality effects of blended, recovered chrome-fresh chrome mixture used as a primary tanning agent.

A soda ash-precipitated, filtered and reacidified spent chrome liquor was used to replace 37% of the Cr_2O_3 used in a normal processing run. This represents the maximum "theoretical" recycle that can be calculated from the overall material balance for chrome in our operations. The recovered chrome was blended with fresh chrome and subsequently added in a single feed. Due to the lower basicity of the recovered chrome the quantity of acid used in the test run was correspondingly reduced. Evaluation of the normal process control indicators showed that the "behavior" of this recycled chrome blend was not significantly different than fresh chrome during the hide processor chrome-tanning process. Likewise, chemical analysis of the finished leather indicated no significant differences between the test and control sides. However, chemical analysis of the full thickness blue stock had shown a 7.35% increase in the Cr_2O_3 content of the test sides on a hide substance basis. Upon stratagraphic five-layer analyses, the middle blue-stock layers showed the greatest difference, with the test sides containing 30% more Cr_2O_3 on a hide substance basis, indicating increased chrome penetration for the chrome recycle test run.

The final sort for the subjective parameters of leather quality indicated that the test-sides were considerably softer than the regulars (six pairs out of ten). They were equal for hair cell, finish break, veins, flesh and break. Again, however, the physical testing for stitch tear and grain burst indicated a substantial loss of strength in the test sides. The Satra force decreased from an average 46 kg in the regular sides to 35 kg in the test sides with a corresponding reduction in extension to grain burst from 8.59 mm to 8.12 mm. Likewise, the stitch tear was reduced from 61 lb to 53 lb.

REUSE OF RECOVERED CHROME BY TWO-STAGE CHROME ADDITION

A matched sides leather test using recovered chrome (from soda ash-precipitated chromium hydroxide) to replace 37% of the chrome offered in our normal chrome tannage indicated no deleterious effects when the lower basicity recycled chrome was fed separately before the regular fresh chrome. The total amount of sulfuric acid used was decreased to adjust the acidity of the combined tan liquor within normal limits. Also, the total chrome used was decreased by 5% to compensate for the previously observed increased take-up during tanning.

Chemically, the finished test sides did not differ significantly from the regular sides. Likewise, the subjectively-evaluated leather qualities were equivalent, except that six of nine test sides were noticeably softer than their matching control sides, and four of the test sides were slightly smoother.

In this test, the comparative physical strength of the test sides was improved over our previous chrome recycle test run. The Satra grain burst strengths were found to be equal, while the stitch tear, this time, was better--with the test sides averaging 44 lb vs 40 lb for the controls.

A second matched sides-leather test using a 33% basic recovered chrome liquor to replace 23% of our normal chrome was also conducted. This level is especially significant as it corresponds to the recycle of the chrome from the most concentrated spent chrome fraction (as a reacidified, soda ash-precipitated and filtered chrome) from a previous processing run.

Again, the recovered chrome was fed separately, before the regular fresh chrome, and the acid was decreased to adjust for the difference in basicity. The chrome take-up efficiencies, as calculated from chrome exhaust liquor analyses, were equal.

Chemically, there was no significant difference between the finished test sides and the controls. Analysis of full thickness blue stock after wringing, however, indicated that the test sides contained approximately 10% more Cr_2O_3 (moisture free) than the regulars.

At the final sort five of the nine test sides were improved with the other four judged equal for fat wrinkles. The test sides were also slightly better than the controls for smoothness, softness and flesh, while no difference was observed for break, veins, or weight. The physical strength of the test sides averaged slightly less using the Satra grain burst strength as the criterion (45 kg vs 50 kg). Likewise, the Satra extension was slightly less at an average of 8.30 mm vs 8.52 mm for the controls. The stitch tear strength of the test sides, however, equalled the controls.

REUSE AS MAKE-UP IN REDUCED CHROME PREPARATION

Basic chromic sulfate tanning agents are produced by the reduction of sodium bichromate in acid solution. Most commonly, organic reducing agents such as molasses or corn syrup are used, although other reducing substances including glycerine, alcohol, dextrin, flour or sulfur dioxide have also been used (23). Careful control of all aspects of the bichromate reduction reaction including temperature, rate, reaction time and mixing must be maintained to produce a reduced chrome liquor with uniform tanning activity. Likewise, it is essential that the proportion of chemicals employed remains constant from batch to batch, since even a slight change will significantly affect the basicity and thus the activity of the finished chrome.

One hypothetical equation for the reduction of sodium bichromate by glucose to yield a 33-1/3% basic chrome liquor (similar to the equation expressed by Orthman)(24) is shown below.

$$\underset{\text{(Sodium Bichromate)}}{4\ Na_2Cr_2O_7 \cdot 2H_2O} + \underset{\text{(Sulfuric Acid)}}{12\ H_2SO_4} + \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Water)}}{58\ H_2O} =$$

$$\underset{\text{(Sodium Sulfate)}}{4\ Na_2SO_4 \cdot 10\ H_2O} + \underset{\text{(Carbon Dioxide)}}{6\ CO_2} + \underset{\text{(33-1/3\% basic chromic sulfate)}}{8\left[Cr\ (OH)\ (H_2O)_5\right]\left[SO_4\right]}$$

In practice, the proportions of reactants vary considerably from these theoretical quantities. The "hydrated chrome" thus formed is actually composed of a multiplicity of chromium complex salts whose molecular species probably include the one for 33-1/3% basic chromic sulfate hydrate shown above. The corresponding Theoretical formula for 48.5% basic chromic sulfate hydrate is:

$$\left[Cr(OH)_{1.455}\ (H_2O)_{4.545}\right]\left[SO_4\right]_{0.7725}$$

This mathematical model shows a decrease in hydroxylation vs the 33.3% basic chrome species.

In a typical production-scale "chrome boil" 5,000 lb of hydrated sodium bichromate is reduced by corn syrup to produce a 48.5% basic chrome liquor. After dilution of the sodium bichromate to 1,575 gallons, 4,300 lb of 66° Bé sulfuric acid is added. Using the heat of dilution of the concentrated acid to initiate the reaction, corn syrup equivalent to 1,070 lb of sugar is metered into the reaction medium at a sufficient rate to maintain a gentle boil. After sugar addition is complete, a small amount of sodium bisulfite is added to insure complete reduction to tri-valent chromium. Before any batch of prepared chrome is released for subsequent use, it is tested and must show a zero hexavalent chromium result. The approximate "chrome boil" yield is 1,700 gallons of stock chrome liquor containing 1.5 lb Cr_2O_3 per gallon.

Since our recovered chrome liquor analyses at approximately 0.6 lb Cr_2O_3 per gallon (0.4 lb Cr/gal), either further concentration, or blending with high concentration chrome liquor, or fortification with spray-dried chrome sulfate is required before the material can be fed back into the "normal" chrome distribution-leather production system.

In practice, we employ the first of these techniques by utilizing the energy of the sugar-sodium bichromate redox reaction in an augmented chrome boil.

Recovered, acidified chrome sulfate from the alkali precipitation-filtration process was used as a portion of the initial diluent in a typical chrome boil. Because of the lower basicity of the recovered chrome the amount of acid normally used can be reduced, taking a credit for the excess acidity.

No major differences in the conduct of the boil for either lime-precipitated or soda ash-precipitated recovered chrome were observed.

Augmentation with recovered chrome containing as much as 17% of the Cr_2O_3 content of a "normal" chrome boil produced a high concentration chrome liquor which analyzed within the desired (48-49%) basicity range. Dilution of the chrome liquor to the normal stock concentration enabled subsequent recycle of the chrome without modification of the tanning process.

SECTION X

HYDROGEN SULFIDE CONTROL

TOXICITY

Hydrogen sulfide is a highly toxic colorless gas which, although mal-odorous in low concentrations, rapidly becomes odorless at physiologically-active concentrations. It is both an irritant and an asphyxiant. Exposure to concentrations as low as 20-150 ppm may cause eye irritation, while slightly higher levels may cause respiratory irritation and lung edema. A 30 minute exposure to 500 ppm of hydrogen sulfide may result in dizziness, headache, staggering, loss of consciousness, diarrhea, dysuria, bronchitis and bronchopneumonia. Finally, exposure to 800-1000 ppm can be fatal in 30 minutes or less (25).

Hydrogen sulfide in solution exists in equilibrium with both sulfide and sulfhydrate ions according to the following relationship:

$$H_2S \rightleftharpoons HS^- + H^+$$

$$HS^- \rightleftharpoons HS^- = S^= + H^+$$

Normally, below pH 12, the equilibrium concentration of sulfide ion is extremely low, whereas relative concentrations of H_2S and HS^- are effectively a function of pH. The extent of hydrogen sulfide occurrence in solution can be calculated from the first ionization constant for the dissociation, as follows:

$$\log \frac{[HS^-]}{[H_2S]} = pH - pK'$$

While the value of pK' varies slightly with the ionic strength of solution, at 25°C, 7.0 (26) is a good approximation for exemplary calculations. Table 38 shows expected proportions of hydrogen sulfide at various values of pH (27).

TABLE 38. PROPORTIONS OF DISSOLVED SULFIDE PRESENT AS H_2S

pH	Proportion as H_2S
10.0	0.001
9.0	0.010
8.0	0.091
7.0	0.50
6.0	0.91
5.0	0.99
4.0	0.999

Above pH 9.0 the relative concentration of hydrogen sulfide is insignificant. As the pH is reduced to 7.0, however, approximately half of the hydrosulfide ion species is converted to hydrogen sulfide, and at pH's less than 7.0, hydrogen sulfide predominates.

Hydrogen sulfide is moderately soluble in water (3,175 mg/l @ 25° C). It does exert a significant partial pressure, however, even at very low solution concentrations. Only 1 mg/l of hydrogen sulfide (as $S^{=}$) in solution (25° C), for example exerts a partial pressure of 0.0024 mm of mercury (28), equivalent to 315 ppm of H_2S by volume. The H_2S concentration in the air increases proportionally with solution concentration.

Since the pH of unhairing solutions generally exceed 11.5-12.00, the dissociation equilibrium is shifted far to the right and the solution concentration of hydrogen sulfide in these lime-sulfide wastes is inconsequential. If the pH in these solutions is reduced, however, by chemical additions during the process or due to the inadvertent mixing with acid wastes in plant sewers, the relative concentration of hydrogen sulfide may increase drastically. The resultant release of hydrogen sulfide gas to the atmosphere could be extremely hazardous!

IN-HOUSE CONTROL

Since no practicable alternative to the alkali-sulfide method of unhairing currently exists, every tanner must maintain rigorous control over the handling of all sulfide-containing raw materials, process liquors, and waste streams. Required control measures include (but certainly are not limited to):

Proper Identification, Storage and Transfer of Hazardous Chemicals

In the recently proposed City of Milwaukee Code revision for "Labeling of Hazardous Materials Storage Systems," (modeled from a Pfister & Vogel "in-house" system) all hazardous materials receiving pipelines, storage tanks and transmission lines should be labeled with appropriate DOT labels, generic names and directional arrows. Each receiving pipeline connection must be padlocked with a different lock, and each key must be clearly identified and secured in a remote area with 24 hour supervision. Finally, all connecting to plant receiving lines should be done under the control of duly trained and competent plant personnel.

Training

All employees who use hazardous materials must be adequately trained in safe handling procedures. This training, in addition, should include an explanation of the consequences of careless use of the materials, a demonstration of the proper use of personal protective equipment, emergency egress procedures, and the insistence that safe operating practices must not be compromised under any circumstances.

Adequate Ventilation

During the "deliming" step of the beamhouse-tanyard process, the designed reduction in pH may generate hydrogen sulfide from the reaction of residual sulfides in the hides. Administrative and engineering controls must be implemented to limit employee exposure within OSHA requirements. Such controls may require efficient exhausting of hydrogen sulfide from the process area, dilution with make-up air, confining the reaction to a closed system and/or finally, limiting the amount of time any person may work in the contaminated area.

Process Drain Controls

Wastewater "dumps" from process operations must be coordinated to preclude the simultaneous discharge of "incompatible" unhairing wastes with spent pickle or spent chrome liquors to open plant sewers or treatment facilities.

Monitoring Work Areas

An effective and convenient tool for determining hydrogen sulfide gas concentrations in the working environment is the Drager Multigas Detector which consists of a 'fixed-volume", bellows pump and a chemical packed glass tube through which the air sample is drawn. In the Dräger Tube 5/b hydrogen sulfide discolors the lead-acetate in the tube; and the tube is calibrated so that the length of the stain is proportional to the H_2S concentration in the air. The method is rapid and the equipment is portable. Thus, for a quick approximation of hydrogen sulfide by grab sample analysis the tube-type detector is invaluable.

When significant concentrations of hydrogen sulfide can be generated without warning in confined working areas, a continuous, automatic monitoring system should be employed. At the Pfister & Vogel Tanning Company, a Bacharach H_2S Continuous Gas Monitoring System was installed in our "Sewer-House", the last point-on-site before all wastes are screened and discharged into the municipal sewage system. A low level alarm relay is set at 20 ppm (acceptable ceiling concentration) and is connected to a flashing yellow light. If the level exceeds 50 ppm ("Acceptable maximum peak above the ceiling concentration for an 8-hour shift"), a high level alarm relay sets off a warning horn. Workers are instructed to evacuate the area within 10 minutes after a low-level alarm, and immediately for a high-level alarm. Additionally, all persons working on the lower level (plus a "safety man" on the ground level) are required to wear supplied-air type respirators, regardless of the presence or absence of hydrogen-sulfide in the ambient atmosphere.

SEWER HOUSE CONTROL MEASURES

As our conversion from a "hair-save" to "hair-burn" process effected substantial increases in our sewage sulfide loadings, while dramatically reducing the alkalinity (the pH of 24 hour-composited in proportion-to-flow total tannery effluent samples were reduced from approximately 12.0 to 9.8) and volume of our effluent, it became increasingly evident that the generation of hydrogen sulfide gas in our sewers and in our Sewer House (the building which houses our effluent screen and sewage pumps) could reach serious levels. The probability of acidic waste streams combining in common sewers with sulfide-bearing wastes increased dangerously. To protect personnel responsible for maintenance of the Sewer House from excessive exposure to hydrogen sulfide, the following precautionary measures were instituted (in addition to the installation of the automatic continuous monitoring system and the required use of respiratory protective equipment):

1. The levels of the sewage pump on-off float switches were adjusted to increase the pump-on-frequency, thus reducing the volume of wastewater retained in the sump, and minimizing the potential for hydrogen sulfide formation.

2. The effective-volume dimensions of the sump were changed to further reduce retention time within the Sewer House.

3. Ventilation was increased by installation of a blower to supply heated make-up air to the lower level of the Sewer House.

4. An Emergency Button integrated with the In-Plant Emergency Alarm System was installed, and supervisory personnel were instructed in the special precautions required of their response to a Sewer House Emergency.

In addition to the measures instituted in the Sewer House, numerous controls were required in the lower tannery. To reduce their retention, within the work area, some of the sewers in the lower tannery were reconstructed and/or rerouted. Although effluent volume-reduction was a primary objective of the grant program, we found it necessary, ultimately, to put back almost 300,000 gpd of fresh water as sewer flushes to provide sufficient dilution to maintain a free-flowing condition.

To prevent the dangerous mixing of acid-containing wastes with sulfide-bearing waste fractions, an inter-connected system of "drain warning flashers" was installed to synchronize the discharge of incompatible waste fractions. Process revisions require each operator to turn on the drain warning flasher during three critical drains. If the flasher is already on he may not proceed until he identifies the existing drain warning. If his intended drain is compatible with the extant drain, he may proceed. If the drain is not compatible, however, the operator must wait until the in-process drain is completed and the Drain Warning Flasher is shut off.

Finally, a respiratory protective program has been established for emergency protection against hydrogen sulfide. To comply with OSHA recommendations, the following programs have been instituted:

1. Instruction (written and verbal) and training of personnel in the proper use of respirators and their limitations.
2. A regular schedule for inspection, repair, cleaning and disinfection of respirators.
3. Storage of respirators in a convenient, clean and sanitary location.
4. Surveillance of work area conditions and degree of employee exposure.
5. Periodic review of respirator user's medical status.

Canister-type gas masks have been located in the lower tannery for emergency egress in case of any hydrogen sulfide "accident." Also, two 30-minute duration, self-contained breathing apparatus have been located in our Power Plant to insure the continued operation or orderly shutdown of plant energy facilities during such an emergency. All regular power-house personnel and all technical and engineering supervisors have been trained in their proper use.

HIDE PROCESSOR DRAIN MANIFOLD

A drain manifold has been incorporated at each hide processor to segregate waste fractions for subsequent pretreatment, reuse or discharge to the sewer. This manifold provides four pumping options:

1. Recirculate process solutions from the rear of the unit to the front of the unit.
2. Discharge waste solutions directly to the sewer.
3. Divert sulfide-containing wastes to the hair-burn header for transfer to the Sulfide Oxidation System.
4. Divert spent chrome wastes to the Chrome Recovery System.

The hair-burn drain line from each hide processor is connected to a common header line leading to the Sulfide Oxidation System. Similarly, the spent chrome drain lines are connected to a Spent Chrome Header leading to the Chrome Recovery System. At present, selection of the proper drain mode and valve configuration is an operator responsibility.

To prevent a catastrophic accident (which could result from the inadvertent mixing of process wastes within the hair-burn or spent chrome collecting facilities) continuous automatic, in-line, pH monitors have been installed (with Ultrasonic electrode cleaning devices employed to reduce electrode fouling). If the pH in the Spent Chrome Header goes above 4.5 a preset relay closes an automatic air operated valve located just ahead of the collection tank, and a warning alarm sounds. Likewise, if the pH in the Hairburn Header drops below 10.0, an automatic valve closes and the alarm sounds. The "closed valve-alarm" continues until the pH in the header pipe is restored to the acceptable level, and the drain-collection system is re-set.

SECTION XI

SULFIDE OXIDATION IN UNHAIRING WASTES - FEASIBILITY STUDIES

LITERATURE REVIEW

Sodium sulfide and sodium sulfhydrate are widely used in the Tanning Industry, to remove hair from the hides and skins prior to tanning. The waste waters discharged from the unhairing operation, therefore, contain substantial quantities of sulfide ion, sometimes exceeding 5,000 mg/l. When these wastes are discharged to a sewerage system and mixed with acidic wastes such that the pH drops below 9.0, hydrogen sulfide gas can be produced.

Bailey (29) reports that sulfide limitations of 0-20 ppm are generally imposed by authorities to avoid the build-up of dangerous concentrations of hydrogen sulfide in sewerage systems. A secondary concern for establishing sulfide limitations is the bacterial oxidation of sulfide to sulfuric acid which can cause crown corrosion in concrete sewers.

The effect of sulfide on biological treatment usually becomes relevant only for "on-site" treatment of tannery wastes. vanVlimmeren (30) reports that while stream concentrations of 10 mg/l or less can be toxic to fish, it is erroneous to conclude that such low levels of sulfide are also toxic to biological treatment system organisms. In fact, sulfide concentrations as high as 50-100 mg/l do not inhabit biological waste treatment operations.

The A. C. Lawrence Leather Company (31) demonstrated on a pilot scale that 24-hour dosages of 100 ppm of sulfide caused no problems in the operation of an activated sludge unit. A two-hour shock loading of 400 ppm failed to damage the activated sludge. According to Bailey (32), while one-hour shock loadings of 250 mg/l of sulfide showed negligible deterioration of an activated sludge system, the level that could be tolerated on a continuous basis was much lower. Aulenbach and Heukelkian (33) concluded that sulfide concentrations up to 25 mg/l were tolerable in activated sludge and up to 50 mg/l could be handled for short intervals. Lawrence and Rudolfs (34) reported a reduction in gas formation when anaerobic digester feed sulfide concentrations were in the 150-200 mg/l range.

Numerous treatment procedures have been proposed to reduce or eliminate sulfides from unhairing wastes. Bailey (35) reports that in Poland, chemical treatment of tannery effluent by coagulation with ferrous sulfate results in 100% reduction in sulfide. Further, the Institute in Lódź has demonstrated 100% reduction in sulfide by activated sludge treatment.

In South Africa (36), eight hours of paddling during the liming process with manganous sulfate as a catalyst (100 ppm Mn) reduced the sulfide level from 431 to 200 ppm. Oxidation of spent lime liquors using manganous sulfate catalysis, nearly completely oxidized the sulfides within a reasonable time. vanVlimmeren (37) reported 95% reduction of sulfide *in situ* in unhairing vats or drums by addition of 200 g/m^3 of manganous sulfate after unhairing is completed, when followed by an additional three hours of paddling or drumming. Separate paddle oxidation of spent unhairing liquors only resulted in 90% reduction after four hours of paddling. A 36% reduction in alkalinity was also observed. Eye and Clement (38) investigated the laboratory scale oxidation of sulfide in lime-sulfide solutions using several oxidizing agents. Ozonation was the most effective method but investigations were limited by lack of an effective contact device. Of the catalyzed air oxidation systems studies manganous sulfate was found superior to trivalent chromium but inferior to potassium permanganate. The latter was found to react as a primary oxidant as well as a catalyst for air oxidation of sulfides. Optimum sulfide oxidation using the air-potassium permanganate system occurred at a manganese-to-initial sulfide ratio of 0.15.

Chen and Morris (39) investigated a number of metal ions as catalysts for the oxidation of sulfides. The order of effectiveness was $Ni^{+2} > Co^{+2} > Mn^{+2} > Cu^{+2}$ in the mildly basic pH range. A two-fold increase in the concentration of Ni^{+2} from 5×10^{-5}M to 10×10^{-5}M not only increased the rate of oxygen uptake but also effected a change in the stoichiometry, reducing the oxygen requirement from 0.8 moles O_2 per mole of $S^=$ to 0.6 moles O_2 per mole $S^=$. Krebs (40) showed that Mn^{++} was the most effective catalyst for air oxidation of sulfides in more alkaline solutions. Bailey (41) indicated that in Switzerland, where a reduction in sulfide in tanning effluent to less than 0.1 mg/l was required, liming effluents were treated by manganese catalyzed air oxidation using floating turbine aeration. While the manganese catalyst has been shown to concentrate in the foam layer, this problem is less severe with surface aeration than when diffused-air aeration is employed. Black and Goodson (42) reported that sulfides present in natural waters at concentrations of 1.90-5.65 mg/l can be oxidized by chlorine to sulfur and sulfate end-products. The stoichiometry of the redox reaction is highly dependent upon pH. Mole ratios of chlorine reacted to sulfide reacted varied from approximately 3.4 at pH 5 to approximately 1.8 at pH 8.

LAB-SCALE STUDIES

Lab-scale familiarization experiments using potassium permanganate catalyst were conducted in a 1,000 ml pyrex beaker with a high speed laboratory stirrer as the aeration device.

A sample of unhairing waste was composited from the hair-burn drain and subsequent washes from a typical hide processor run and passed through a 30 mesh screen to remove coarse suspended solids. To an aliquot of the screened waste (2,120 mg/l sulfide) a 4% solution of potassium permanganate equivalent to a reaction mixture Mn++ concentration of 212 mg/l (10% of the initial sulfide) was added. "Once-through" oxidation resulted in an 80% decrease in sulfides after one hour, as measured by the Iodimetric Method outlined by Skoog and West (43). The progress of the reaction is shown in Figure 21.

Severe foaming occurred during the oxidation run. The apparent failure to achieve better than 80% reduction in sulfide content is believed due to the non-specificity of the Iodimetric Method used as the indicator of the oxidation progress, rather than a characteristic of the oxidation process/equipment. Therefore, in subsequent oxidation runs (lab, pilot and full-scale) a titrimetric method employing a standard solution of potassium ferricyanide as titrant was employed (Society of Leather Trades' Chemists Method No. SLM 4/2).

Further bench-scale oxidation runs were conducted using screened, undiluted unhairing waste which analyzed at 4,210 mg/l $S^=$. Potassium permanganate solution equivalent to 20% of the initial sulfide (842 mg/l Mn^{++}) was added. After 60 minutes of aeration no sulfide could be detected by the Society of Leather Trades' Chemists Method. The reaction mixture changed from an initial brownish green color to a light tan at the end of the 60-minute aeration period. Approximately 30 minutes after turning off the aerator an aliquot of the resuspended mixture analyzed at 40 mg/l $S^=$. Within 75 minutes after discontinuing aeration a concentration of 56 mg/l $S^=$ was observed.

For the third run, a 10% catalyst ($KMnO_4$ solution) dosage was used and 75 minutes of aeration was required to reduce the sulfide from an initial concentration of 4,210 mg/l to zero. An observed increase in pH from 11.9 at 40 minutes to 12.25 at 75 minutes corresponded with the noted color change from green-brown to light tan.

These bench scale "probe" experiments suggested that further investigation of the various parameters for manganese catalyzed air oxidation of sulfides in unhairing wastes was warranted. The topics for further investigation were:

1. Rate of oxidation
2. Types of aeration devices
3. Effect of screenable solids on sulfide oxidation
4. Effect of initial sulfide on rate
5. Foaming
6. The "reappearance" of sulfide
7. Color changes
8. pH change
9. Catalyst type and dosage

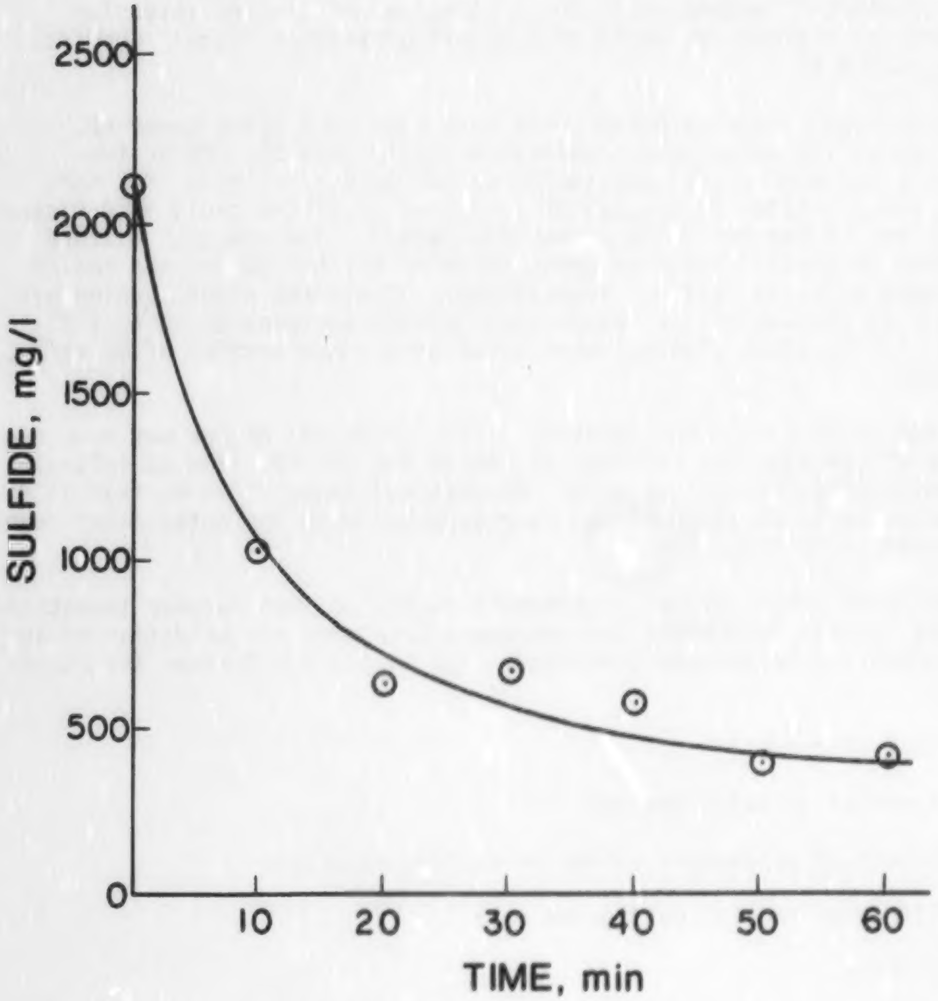

Figure 21: BENCH-SCALE OXIDATION OF SULFIDES IN UNHAIRING WASTES.

PRESCREENING HAIRBURN WASTES

Two commercially available wastewater screens were tested for the pretreatment of unhairing wastes prior to manganese catalyzed air oxidation. Neither the Bauer Hydraseive nor the Dorr Oliver 300° Pressure Screen performed satisfactorily under the conditions encountered. The most serious shortcomings were blinding of the Hydraseive and excessive sludge volume from the Dorr Oliver Screen. Fortuitously, subsequent oxidation runs demonstrated that prescreening did not significantly improve sulfide oxidation rates.

The Bauer Hydraseive tested was an 18 inch wide gravity screen with interchangeable screen surfaces having openings ranging from 0.010 inches to 0.080 inches. Undiluted hairburn liquor was pumped over the screen at the rate of 35-50 gpm (1.94-2.78 gal per inch of screen width). The screen surfaces tested (i.e., 0.020", 0.030", and 0.040") all immediately blinded.

In another run, 3,350 gallons of unhairing waste including subsequent washes from a typical hide processor run were collected and equalized. This diluted waste was then pumped over the Hydraseive fitted with a 0.20" opening screen at an average rate of 47 gpm. The feed to the screen contained 25,700 mg/l of suspended solids and the screened waste analyzed at 24,400 mg/l. Approximately 100 gallons of sludge containing 9.5% total solids were collected. Thus, a suspended solids reduction efficiency of only 5% was observed.

Parallel feasibility studies were conducted using a Dorr Oliver 300° pressure screen with slot openings of 300, 150 and 75 microns. During the initial studies, 3,800 gallons of diluted unhairing wastes, containing approximately 25,000 mg/l of suspended solids, were pumped from a hide processor to the collection vessel. Using a screen with 300 micron openings, a sludge fraction equivalent to approximately 5% of the feed volume was generated. Visual comparison of the sludge and effluent from the screen indicated that there was no substantial solids disproportionation. Using a screen surface with 75 micron openings, an unacceptable sludge volume of greater than 50% of the feed was collected.

At a slot opening of 150 microns, however, a distinct separation was noted. Sludge volumes were estimated at 10-20% of the feed.

Continued investigations were conducted using the 150 micron opening. Unhairing waste including spent unhairing liquor and subsequent washes were collected and fed to the pressure screen at a rate of 125-150 gpm at 50 psi (feed suspended solids = 24,600 mg/l in 3,800 gal). Approximately 500 gallons of sludge were collected containing 65,600 mg/l of suspended solids. Thus, 35% of the suspended solids was concentrated into a sludge volume equal to roughly 13% of the original volume.

Therefore, while a significant solids separation has been demonstrated, the large volumes of sludge generated could create a more serious disposal problem than the discharge of the untreated unhairing wastes directly to the sewerage system.

STOICHIOMETRY OF SULFIDE OXIDATION

The concentrations of sulfide species in water are defined by the following chemical equilibria:

$$H_2S = H^+ + HS^-;\ K_1 = \frac{(H+)\ \ (HS-)}{(H_2\ S)}$$

$$HS^- = H^+ + S^=;\ K_2 = \frac{(H+)\ \ (S^=\ )}{(HS\ -)}$$

While the first ionization constant, K_1, is well established at 7.02, the second ionization constant, K_2, can only be estimated to lie within the 12.35 - 15 range (44). Simple calculations show that within the pH 7.0 - 12.5 range, the dominant sulfide species is the HS^- ion.

Sulfide oxidation by elemental oxygen may consume or generate hydrogen ions to produce several possible reaction products (45):

$$HS^- + 1/2\ O_2 + H^+ \longrightarrow H_2O + S$$

$$HS^- + O_2 \longrightarrow H_2O + 1/2\ S_2\ O_3^=$$

$$HS^- + 2O_2 \longrightarrow SO_4^= + H^+$$

Thus, the oxygen requirement as predicted by these stoichiometric relationships ranges from 0.5 moles to 2 moles oxygen per mole of sulfide.

As demonstrated by Chen & Morris (46) for the Ni^{+2} catalyzed air oxidation of sulfides, an increase in the catalyst concentration not only accelerates the initial rate of oxygen uptake but also changes the stoichiometry of the reaction. Thus, when the catalyst concentration was doubled from $5x10^{-5}$ to $1x10^{-4}$ molar, sulfide converted to elemental sulfur doubled from 40% to 80%, the remainder being converted to thiosulfate. Likewise, the oxygen requirement was reduced from 0.8 to 0.6 moles O_2 per mole of sulfide consumed.

From lab-scale studies using sulfide unhairing wastes, it is evident that the oxygen requirements for manganese catalyzed-air oxidation of sulfides in unhairing wastes lie within the 0.6 to 1.0 lb O_2 per lb $S^=$ range.

To test the effect of sulfide concentration on this redox system, varying aliquots of hair-burn waste were adjusted to 150 ml and placed in stoppered quart containers along with 10% Mn^{++} as manganous sulfate solution. Half of these samples were analyzed for residual sulfides after 6 hours of agitation on an automatic shaker. The other half were shaken intermittently over a 24-hour period and then promptly analyzed for sulfides. By calculating the amount of oxygen initially available in the sealed containers (47), (Table 39) the weight ratio of oxygen-to-sulfide reacted was determined.

When the initial concentration of sulfides present was 1,670 mg/l, the

TABLE 39. OXYGEN UPTAKE FOR SULFIDE OXIDATION

Sample	Shake time, hr	Waste volume, ml	Mn^{++}, mg	Initial $S^=$, mg	Final $S^=$, mg	$\Delta S^=$, mg	$O_2/S^=$
1	6	5.85	2.5	25	0	25	-
2	6	58.5	25	250	35	215	1.01
3	6	117	50	500	226	274	0.80
4	24	5.85	2.5	25	0	25	-
5	24	58.5	25	250	33	217	1.00
6	24	117	50	500	153	347	0.63

Air offered = 0.795 liters

Oxygen offered = 218 mg O_2*

Total solution volume = 150 ml

* One liter of air contains 273 mg O_2 @ STP, Fair Guyer & Okun, Vol. 2, Chap. 35, p. 24.

$O_2/S^=$ ration was 1.0 both after 6 hours and after 24 hours. When the initial sulfide concentration was increased to 3,340 mg/l, this ratio decreased to 0.80 lb O_2/lb $S^=$ after 6 hours and 0.63 lb O_2/lb $S^=$ after 24 hours.

Thus, it is apparent that sulfide concentration substantially effects the stoichiometry of this redox reaction.

SULFIDE OXIDATION BY PADDLE AERATION

On completion of the bench-scale studies of the oxidation of sulfides in unhairing wastes, a pilot-scale oxidation system was employed to observe the effect of several parameters on the sulfide oxidation process. Primary emphasis during this phase of the program was placed upon the determination of the effects of the physical form of the catalyst feed, catalyst dosage and valence on the air oxidation of sulfides. The effect of initial sulfide concentration was investigated, as well as the phenomena of foaming, color and pH change.

These pilot studies were conducted in a pair of tannery paddle vats having surface dimensions of 9' x 14' with a capacity of approximately 4,000 gallons each.

The recirculating-drain pump servicing each hide processor was used to transfer the wastes through specially installed wastewater collection lines to the paddle vats.

Initial oxidation runs in the paddles were conducted using potassium permanganate catalyst added as a single dry feed at the start of the run. The unhairing wastes consisted of mixtures of concentrated hair-burn liquors plus subsequent washes. Batch volumes of 3,100-3,300 gallons were used in all but a few paddle-aeration runs involving sequential oxidations. For the first five runs, an average time of 2.75 hours was required to reduce the sulfide from an average initial level of 1,400 mg/l to "zero". The mean rate of disappearance of sulfide over the five runs was 14.2 lb $S^=$/hr. As shown in Table 40, initial sulfide concentrations varied from 1,040 mg/l to 1,750 mg/l while the mean rate of oxidation and reaction time varied from 9.05 - 18.5 lb $S^=$/hr and 1.5 - 3.5 hours, respectively.

During oxidation runs 1, 2 and 4, severe foaming necessitated the use of an antifoam (Dow Corning DB-31) to contain the reaction mixture within the paddle vat (even though one foot of freeboard was provided). An antifoam dosage of 20-60 ppm applied as a 1:1 water emulsion and sprayed over the surface of the foam, adequately controlled foaming for up to 30 minutes.

As the sulfide oxidation progressed, a gradual change in the color of the mixture occurred. The initial dark brown color of the hairburn-manganese catalyst mixture turned to a deep olive brown which eventually lightened to a celery green and finally to a beige color. Appearance of the beige color signaled the approach of the "zero" level.

After a "zero" sulfide reading was recorded, samples of the aerated mixtures were left undisturbed at room temperature for 24 hours. These samples reverted to their earlier brownish-green colors and sulfide levels ranging from 22-73 mg/l were regenerated. Comparison of samples stored in open containers vs air-tight containers indicated no significant difference in sulfide. Thus, this reappearance phenomenon is probably independent of the presence of an air-liquid interface.

TABLE 40. SULFIDE OXIDATION BY PADDLE AERATION

Run	Initial Sulfide mg/l	Initial Sulfide lb	Time,min	Rate Mean,lb $S^=$/hr	Rate Max. 15 minute-incremental,lb $S^=$/hr
1	1,530	40.8	150	16.3	29.8
2	1,750	46.6	180	15.5	36.2
3	1,510	40.3	210	11.5	38.5
4	1,040	27.8	90	18.5	53.1
5	1,200	32.0	210	9.05	19.2

$Mn^{++}/S^= = 0.15$

Volume = 3,200 gal

The redox curve for Run No. 3 which is depicted in Figure 22 is typical of results obtained for the five potassium permanganate catalyzed oxidation runs. The outstanding characteristic of this family of curves is the extremely high initial rates of sulfide disappearance. Thus, while the mean rate of disappearance of sulfide in Run No. 3 was 11.5 lb $S^=$/hr, a maximum incremental rate of 38.5 lb $S^=$/hr was observed during the initial 15 minutes of the reaction. These initial rate maxima which are consistent with the observations of Eye and Clement (48) are probably due to direct chemical oxidation of the sulfide by potassium permanganate--an extremely strong oxidizing agent. As the potassium permanganate is reduced, the manganous hydroxide floc which is formed provides the catalytic surface for the continued air oxidation of the sulfide at a slower rate. The mechanism for this catalyzed air oxidation probably employs the same oxygenated manganous species involved in the Winkler dissolved oxygen test (49, 50, 51).

When dry manganous sulfate replaced potassium permanganate as catalyst a substantial difference in the rate curve was observed. In runs No. 6 and No. 7 manganous sulfate monohydrate equivalent to an initial manganese-to-sulfide ratio of 0.15 was added to the aeration mixture at time zero.

The rate of oxidation which averaged 11.6 lb $S^=$/hr over the two runs was slightly lower than that observed for potassium permanganate catalysis

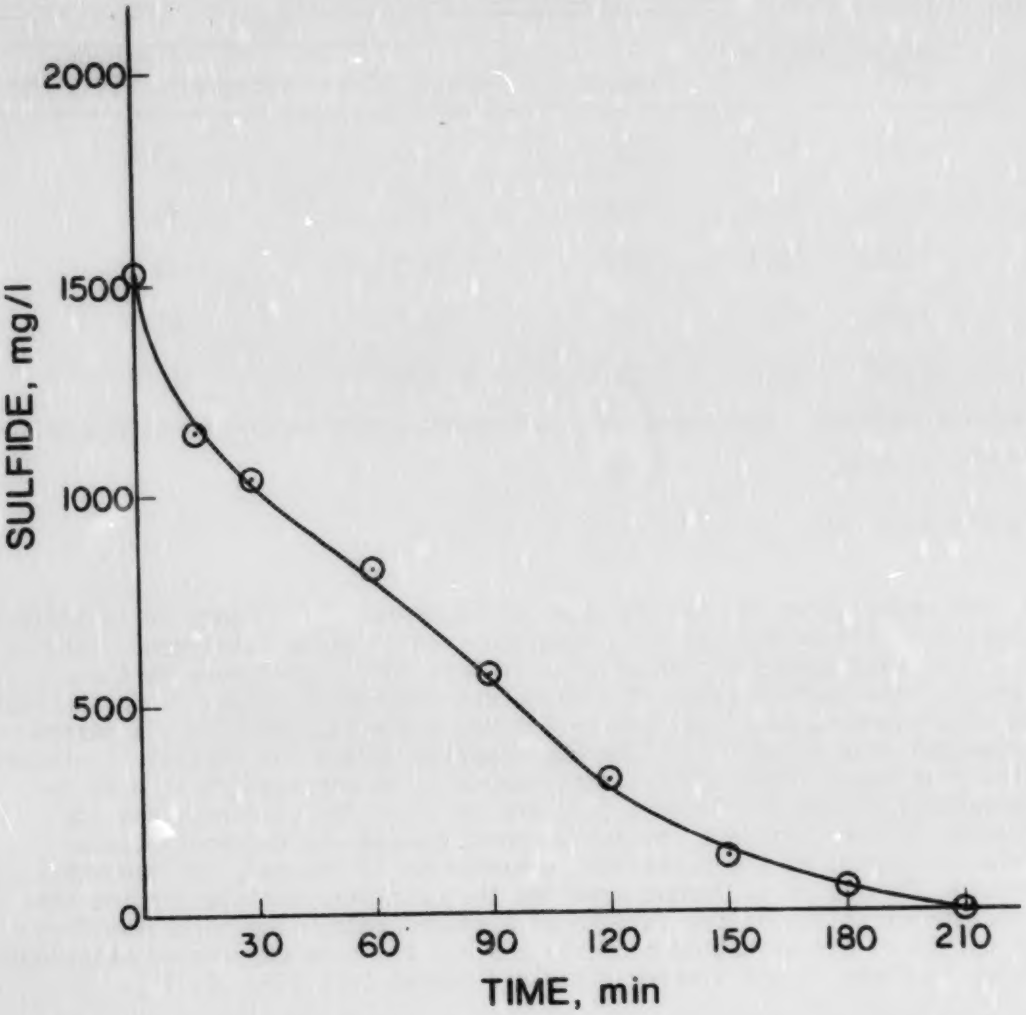

Figure 22: OXIDATION OF SULFIDES BY PADDLE AERATION (Run No. 3)

(14.2 lb $S^=$/hr). The maximum incremental rate, however, which averaged 17.4 lb $S^=$/hr for the two runs was less than half that observed with potassium permanganate. Contrary to results obtained using potassium permanganate as catalyst, the rate maxima occurred during the third hour of aeration after the sulfide had been reduced to approximately half the initial levels.

Therefore, while manganous sulfate effects a substantial change in the shape of the rate curve vs potassium permanganate, potassium permanganate is only 25% more effective when used dry in a batch oxidation system.

Further oxidation runs were conducted in paddles using a solution of manganous sulfate as catalyst. At a manganese-to-sulfide ratio of 0.15 with all of the catalyst added to the reaction mixture at time zero, the average rate of sulfide oxidation for two runs was 18.7 lb $S^=$/hr with maximum incremental rates averaging 29.5 lb $S^=$/hr.

In three subsequent runs manganous sulfate solution was added in three feeds at 30-minute intervals to bring the manganese concentration to 0.15 of the initial sulfide content. The observed mean rates averaged 18.1 lb $S^=$/hr, while the maximum incremental rate averaged 26.2 lb $S^=$/hr.

Thus, introduction of the manganous sulfate catalyst in solution resulted in a substantial improvement over dry catalyst feeds.

There does not appear to be a substantial difference between the use of catalyst in a single solution feed vs addition in three feeds.

Additional paddle runs were conducted to determine the effect of manganous sulfate dosage on sulfide oxidation. Catalyst was fed in solution in a single feed at time zero. The data illustrated in Table 41 demonstrate that reducing the catalyst-to-sulfide ratio from 0.15 to 0.10 or less adversely affects the kinetics when catalyst is added in a single feed. However, no significant advantage was demonstrated by increasing the ratio from 0.15 to 0.20. Thus, the optimum manganese-to-sulfide ratio lies within the 0.10-0.15 range when manganous sulfate solution is added in a single feed in paddles.

Another experiment using the paddle aerator was conducted to determine the catalytic activity of used manganese sludge in a subsequent sulfide oxidation run. This experiment demonstrated that day-old recovered sludge does exhibit catalytic activity when it is mixed with fresh hair-burn wastes for subsequent aeration.

Approximately 3,200 gallons of hair-burn wastes having an initial sulfide concentration of 1,840 mg/l were aerated using a catalyst dose of 20% of the initial sulfides (catalyst added in solution). After the oxidation was complete, the mixture was allowed to settle and the supernatant was pumped off leaving approximately one-third of the original volume as sludge. The following day fresh hair-burn waste was added to the settled sludge at a two-to-one ratio. The net sulfide ion concentration of the mixed liquor was 1,540 mg/l. This mixture was aerated without any further addition of catalyst.

The first use of catalyst effected a reduction of the sulfide level to zero in 2.75 hours. The second use of the catalyst in the recycled sludge resulted in complete oxidation of the sulfides in 4 hours. These data contrast to the approximately 9 hours required to reduce the sulfides to zero by aeration without catalyst of any kind.

TABLE 41. EFFECT OF CATALYST DOSAGE ON SULFIDE OXIDATION BY PADDLE AERATION

$Mn^{++}/S^{=}$	Initial Sulfide		Time,min	Rate	
	mg/l	lb		Mean,lb $S^{=}$/hr	Max. 15 minute-incremental,lb $S^{=}$/hr
0.05	2,080	53.7	285	11.3	16.0
0.10	2,040	52.7	195	16.2	23.2
0.15	1,780*	46.4*	150*	18.7*	29.5*
0.20	1,840	47.6	165	17.3	30.4

Volume = 3,200 gal

* average for two runs

FLOATING SURFACE AERATOR

Among the alternative aeration systems investigated for the oxidation of sulfides in unhairing wastes was a floating surface aerator. A two horsepower floating surface aerator manufactured by Aqua-Aerobic Systems, Inc. (Aqua-Jet Mark 2) was installed in one of the paddle vats which had been previously used for paddle aeration. This aerator had a manufacturer rating of 3.9 lb O_2 transferred per nameplate-horsepower in clear water at standard temperature and atmospheric pressure.

After removing the paddle wheel, the aerator was moored with four chains suspended from support beams spanning the vat. Operation of this pilot aeration system provided the information summarized in Table 42 which was used to design full-scale facilities.

In four oxidation runs using this surface aeration system batch volumes averaged 3,300 gallons and initial sulfide averaged 2,580 mg/l (Runs 22, 25, 27 & 29). A manganese-to-sulfide ratio of 0.15 was employed. The manganous sulfate solution was added in three feeds 30 minutes apart. An average of 5.3 hours of aeration was required to reach zero sulfide. A silicone antifoam was added as required to contain the foam within the 1.5 feet of freeboard provided. The mean rate of sulfide reduction over the four runs was

TABLE 42. SULFIDE OXIDATION BY SURFACE AERATION - PILOT SYSTEM

Run	Volume, gal	$Mn^{++}/S^{=}$	Initial sulfide, mg/l	Initial sulfide, lb	Time, min	Rate: mean rate, lb $S^{=}$/hr	Rate: max. incremental rate, lb $S^{=}$/hr	Aerator efficiency: mean eff., lb $S^{=}$/hp-hr	Aerator efficiency: max. incremental eff., lb $S^{=}$/hp-hr
18	3300	0.15	1310	36.0	150	14.4	26.4	7.2	13.2
19	1650	0.15	1280	17.6	90	11.8	19.1	5.9	9.5
20	3300	0.15	620	17.3	120	8.6	12.3	4.3	6.1
21	1650	0.15	2540	35.1	345	6.1	8.2	3.0	4.1
22	3300	0.15	2640	72.8	240	18.2	36.6	9.1	18.3
23	3300	0.15	4980	136.5	900*	9.1	17.0	4.5	8.5
24	3300	0.15	2620	56.1	510**	6.6	9.4	3.3	4.7
25	3300	0.15	2620	71.6	450	9.55	14.2	4.8	7.1
26	3300	0.15	2530	70.8	390	10.9	14.8	5.4	7.4
27	3300	0.15	2540	69.5	390	10.7	21.7	5.3	10.8
28	3300	0.15	5470	121.8	870***	8.4	17.5	4.2	8.7
29	3300	0.15	2520	69.5	210	19.8	34.0	9.9	17.0
30	3800	0.15+	1320	41.8	165	15.1	44.1	7.5	22.0
31	3800	0.15+	930	29.5	105	16.8	30.0	8.4	15.0
32	3800	0.015+	1340	42.4	210	12.1	25.2	6.0	12.6
33	3800	0.10+	2740	86.3	195	26.7	51.8	13.4	25.9

* impeller clogged; final sulfide - 662 mg/l after 900 minutes.

** impeller clogged; final sulfide - 510 mg/l after 510 minutes.

*** final sulfide - 1,010 mg/l after 370 minutes.

14.6 lb/hr for an aerator-oxidation efficiency of 7.3 lb $S^=$/hp-hr. The maximum 30 minute-incremental rate observed was 36.6 lb $S^=$/hr for an incremental aerator efficiency of 18.3 lb $S^=$/hp-hr.

The effect of initial sulfide concentration on sulfide oxidation was measured in subsequent runs maintaining the original batch volume of 3,300 gallons and the manganese-to-sulfide ratio of 0.15. When the initial sulfide concentration was reduced approximately 50% (Run No. 18), the aeration time required to achieve a zero sulfide reading was reduced from 6 to 2.5 hours. A mean sulfide reduction rate of 14.4 lb/hr, equivalent to 7.2 lb/hp-hr was thus observed. A maximum 30 minute-incremental rate of 28.3 lb/hr was recorded.

Further reduction of the initial sulfide, however, to 620 mg/l (Run No. 20) effected a substantial drop in the mean rate to 8.6 lb $S^=$/hr (4.3 lb/hp-hr) and a drop in the maximum incremental rate to 12.3 lb $S^=$/hr with two hours of aeration required.

Hair-burn liquors, as discharged from the hair pulping operation before being mixed with subsequent washes, contain substantially higher waste concentrations. Sulfides in excess of 5,000 mg/l are common, while total solids normally exceed 100,000 mg/l. A 3,300 gallon batch of concentrated hair-burn liquor collected from four process runs was subjected to aeration in the surface aerator system (Run No. 28). Manganous sulfate equivalent to 0.15 times the initial sulfide on a $Mn^{++}/S^=$ basis was added in three solution feeds, 30 minutes apart. The sulfide was reduced from an initial 5,470 mg/l to 1,010 mg/l after 14.5 hours of aeration. Thus, the mean rate of oxidation observed was 8.4 lb $S^=$/hr, equivalent to an aerator efficiency of 4.2 lb/hp-hr. The maximum 30 minute-incremental rate recorded was 17.5 lb $S^=$/hr.

Thus, it is apparent that dilution of unhairing waste from the 5,470 mg/l $S^=$ encountered in concentrated liquors to approximately 2,500 mg/l by including wash waters effects a substantial increase in oxidation rates. Concentrations from 2,500 mg/l down to 1,300 mg/l clearly lie within the optimum range. As further dilution lowers sulfide concentrations to 620 mg/l the rate of oxidation again falls off.

Another experiment using this surface aeration system was designed to determine the effect of basin geometry on the oxidation of sulfides in unhairing wastes.

When the volume was reduced to half of the "normal" volume, doubling the power-to-volume ratio from 0.6 hp/1,000 gal to 1.2 hp/1,000 gal (Run No. 21), nearly 6 hours of aeration were required to reduce the sulfide from an initial 2,540 mg/l to zero ($Mn^{++}/S^= = 0.15$). Thus, the recorded mean rate of oxidation was reduced from 12.8 lb $S^=$/hr at 3,300 gallons to 6.1 lb/hr at 1,650 gallons for an aerator-oxidation efficiency of 3.0 lb/hp-hr. The maximum 30 minute-incremental rate observed was reduced to only 8.2 lb $S^=$/hr equivalent to 4.1 lb $S^=$/hp-hr.

In another run, both the initial sulfide content and the batch volume were reduced to approximately half of the normal levels (Run No. 19) while the 0.15 $Mn^{++}/S^{=}$ ratio was maintained (manganous sulfate in three solution feeds 30 minutes apart). One and one-half hours of aeration were required to reduce the sulfide from 1,280 mg/l to zero.

Thus, at approximately half the normal batch volume (power/volume = 1.2 hp/1,000 gallons) and half the normal sulfide level, the mean oxidation rate dropped to 11.8 lb $S^{=}$/hr from the 14.4 lb/hr observed when half the normal sulfide level was used at a power-to-volume ratio of 0.6 hp/1,000 gallons.

While a substantial reduction in reaction time was observed, this increase in the power-to-volume ratio sacrificed aerator efficiency.

Another experiment was conducted in the surface aeration system using an "uncontaminated" unhairing liquor consisting of 150 pounds of hydrated lime in 3,300 gallons of 2,580 mg $S^{=}$/l sodium sulfhydrate solution (Run No. 26). The temperature of the mixture was adjusted to a typical hairburn waste discharge temperature of 86°F. Manganous sulfate solution was added in three feeds 30 minutes apart at a total $Mn^{++}/S^{=}$ ratio of 0.15. The mixture required 6.5 hours of aeration to reduce the sulfide to zero. The mean rate of sulfide removal was 10.9 lb/hr (5.4 lb/hp-hr) while a maximum 30 minute-incremental rate of 14.8 lb/hr (7.4 lb/hp-hr) was observed. Foaming, throughout the run, was pronounced but did not increase in severity with aeration nor was antifoam required. The color of the reaction mixture varied with aeration time but did not follow the color trend observed during a normal hairburn waste sulfide oxidation. Instead, the initial reaction mixture was a translucent pale yellow separating into a transparent yellow supernatant and a white sludge layer. As the oxidation progressed, the intensity of the supernatant increased and the calcium hydroxide-manganese hydroxide sludge layer turned dark brown. Near the end point of the reaction the intensity of the supernatant decreased until finally when no sulfide could be detected the supernatant was colorless. These results indicate that the complex mixture of dissolved and suspended proteinaceous matter, inorganic salts, greases, alkalis, etc. which accompany the sulfides and hydrated lime present in unhairing wastes does not demonstrably inhibit the manganese catalyzed, air oxidation process.

In one attempt to improve the rather low rate of oxidation (8.4 lb $S^{=}$/hr) observed with concentrated hairburn liquors, concentrated wastes were mixed with previously oxidized unhairing waste, restrengthening the mixture with manganous sulfate catalyst. In this mixture the sulfides were oxidized at substantially higher rates than the concentrated waste alone.

A mixture of 3,300 gallons of hairburn liquor and wash water containing 69.5 lb of sulfide at an initial concentration of 2,520 mg/l was aerated using 15% manganese ($MnSO_4.H_2O$) as catalyst. At an average rate of 19.8 lb $S^{=}$/hr, the oxidation took 3.5 hours to complete. The mixture was then drained to approximately 3,000 gallons and 850 gallons of concentrated hairburn liquor was added. The sulfide concentration of the mixed waste was 1,320 mg/l (Run No. 30). After restrengthening with 15% manganese, the mixture was aerated for 2.75 hours to a zero detectable sulfide level.

This treatment procedure was repeated for four successive runs. The sulfide concentrations after the addition of the concentrated liquor were 1,320 mg/l, 930 mg/l, 1,340 mg/l and 1,160 mg/l, respectively (Runs 30, 31, 32 & 33). In the final run, 50 lb of sulfide was added as a solution of sodium sulfhydrate, increasing the concentration from 1,160 mg/l to 2,740 mg/l. The catalyst dosages for the four runs were 15%, 15%, 1.5% and 10%, respectively. Corresponding average rates of sulfide oxidation of 15.1, 16.8, 12.1 and 26.7 lb $S^=$/hr were observed.

Thus, as these data indicate, concentrated hairburn wastes can be treated at substantially higher rates when they are mixed with previously aerated and oxidized wastes.

These oxidation rates sharply contrast to the aerator manufacturers performance data. After correction for temperature, residual and saturation D.O. under field conditions and α and β according to the commonly accepted formula for aerator sizing (52) (Figure 23) oxygen transfer rates on the order of 4.0 lb O_2/hp-hr are predicted using the conservative assumptions that α and β are unity and the O_2 residual is maintained at 0 mg/l. Even with a minimum observed oxygen-to-sulfide ratio of 0.6 lb O_2 consumed per 1.0 lb sulfide oxidized, the maximum sulfide oxidation efficiency which could be predicted is 6.7 lb $S^=$/hp-hr.

Demonstrated incremental aeration efficiencies as high as 26 lb $S^=$/hp-hr and mean efficiencies as high as 13.3 lb $S^=$/hp-hr sharply contrast this predicted transfer rate for the manganese catalyzed air oxidation of sulfides in unhairing wastes.

Due to the oxygen scavenging nature of both the manganese hydroxide and the sulfides contained in the waste, it is impossible to empirically determine a D.O. saturation value and thus β can only be estimated. Due to the high concentration of dissolved and suspended matter, it is reasonable to expect, however, that β is less than one. The only remaining factor which can be associated with this marked increase in oxygenation rates over specified manufacturer rates for clean water operation is α, the ratio of field O_2 transfer rates to clean water transfer rates. This factor is dependent upon both the stoichiometry of the sulfide oxidation reaction and the oxygen requirement. The authors conclude, therefore, that aeration equipment for the manganese catalyzed air oxidation of sulfides in unhairing wastes may be accurately and conveniently specified in terms of sulfide oxidized per horsepower per hour rather than the conventional O_2 transfer specification.

$$\text{FTR} = \frac{\text{CWTR}\left[(C_{Dc} \times \beta) - C_R\right] \times (1.024)^{T-20}\,\alpha}{C_{sc}}$$

Where;

FTR = Field Transfer Rate, lb/hp-hr

CWTR= Clean Water Transfer Rate, lb/hp-hr

C_{Dc} = Saturation Concentration of O_2 at Design Temp. & Altitude, mg/l

C_R = Residual D.O., mg/l

C_{SC} = Saturation D.O. at Standard Conditions, 9.17 mg/l

T = Temperature, $^{\circ}C$

$\beta = \dfrac{\text{Sat. D.O. in Waste}}{\text{Sat. D.O. in Clean Water}}$

$\alpha = \dfrac{\text{Rate of Transfer of } O_2 \text{ into Waste}}{\text{Rate of Transfer of } O_2 \text{ into Clean Water}}$

$$\text{FTR} = \frac{(3.9\ \text{lb/hp-hr})\left[(7.5\ \text{mg/l} \times 1.0) - 0\ \text{mg/l}\right] \times 1.26 \text{x} 1.0}{9.17\ \text{mg/l}} = 4.0\ \text{lb/hp-hr}$$

Figure 23. Determination of field transfer rate

SECTION XII

SULFIDE OXIDATION SYSTEM DESIGN

CAPTURE OF SULFIDE

The sulfides introduced in tannery operations are concentrated in discrete, beamhouse sub-process solutions. The segregation and collection of the resultant sulfide-bearing wastes remain among the most difficult and unresolved problems in the pretreatment of tannery effluents. Even when modern manufacturing equipment which provides re-circulation and pump-out mechanisms is employed, the major difficulty in collecting sulfide wastes is their widespread occurrence in low-concentration/high-volume wash waters, etc. which, nevertheless, contribute substantially to sulfide loadings. Approximately 40% of the sulfides generated from a single production run may be contained in as little as 700-800 gallons of concentrated unhairing liquor. The capture of 80% of the sulfides requires that more than 5,000 gallons be collected; and to achieve 99% capture, over 13,000 gallons per unit-run must be collected. It has been demonstrated that processing steps after the liming-unhairing operations including bating and pickling continue to extract sulfides from the hides. Their combined contribution equals only 1-2% of the total sulfide discharge, but concentrations as high as 48 mg/l and 10.2 mg/l in the bate and pickle liquors have been respectively recorded. Including these wastes in the sulfide treatment would increase volumes to more than 20,000 gallons per production run.

Table 43 illustrates the relationship between volume collected and sulfide capture for a typical hide-processor run. It is apparent from Table 43 that while 90% of the total sulfide loading is concentrated in the first 6,300 gallons of effluent, only 1% of the sulfide is contained in the last 6,900 gallons. In fact, capturing just the last 4.5% of sulfide increases the volume of effluent to be collected and treated from 8,600 gallons to a total of 20,100 gallons.

Thus, when segregation of waste streams is possible, the volume of sulfide-bearing streams collected for pretreatment will be a first-order function of the effluent limitations set by the controlling regulatory agency rather than cost-effective logic of Table 43 distributions.

At the Pfister & Vogel tannery only 61% of beamhouse-tanyard processing is done in equipment utilizing pump-out systems. The remaining 39% of the lower tannery effluent is discharged via gravity to common tannery sewers. In normal tannery production, necessary process adjustments, "unscheduled" process and/or mechanical upsets, and variability in hide weight, water flow, draining efficiency, etc. are commonplace. The time required for production runs is sufficiently irregular as to preclude absolute control of discharges for sulfide collection by rigorous scheduling, even if diversion of such process effluents through common sewers were practicable. Therefore, that 39% of the total sulfides which are gravity-drained are not considered amenable to pretreatment by segregation and sulfide oxidation.

TABLE 43. CUMULATIVE CAPTURE OF SULFIDES

Production drain sequence	Cumulative wastewater volume, gal	Cumulative sulfide mg/l	lb	% capture
hair-burn	730	6,490	39.4	39.0
↓	1,800	3,780	56.6	56.0
	3,300	2,570	70.7	70.0
	4,000	2,240	74.6	73.9
	5,100	1,870	79.4	78.6
relime	6,300	1,730	90.7	89.9
↓	8,600	1,350	96.4	95.5
	9,400	1,260	98.7	97.8
	12,000	998	99.8	98.8
	13,200	910	100.0	99.0
bate	19,700	615	100.9	99.9
pickle	20,100	604	101.0	100.0

Segregation of the 61% of sulfide-bearing wastes collected through the hide processor pump-out system requires facilities to collect and treat 221,000 gallons per day containing approximately 1,100 lb of sulfide. Alternative levels of sulfide-waste collection and treatment are illustrated in Table 44 (for eleven of Pfister & Vogel's production units).

TABLE 44. ALTERNATIVE LEVELS OF SULFIDE COLLECTION AND TREATMENT

Treatment alternative	Volume, gal/day	Sulfide lb/day	% total loading
A	221,000	1,110	61
B	70,000	1,000	55
C	37,000	780	43
D	8,000	430	24

Sulfide capture requires errorless control of process discharges through operator recognition and execution of the appropriate drain sequences. Absolute control against the mixing of acidic wastes with alkaline lime-sulfide waste streams must be maintained. Thus, pickle and chrome liquors must be collected separately, pre-neutralized or sewered directly to avoid possible generation of hydrogen sulfide within the collection facility. Only alkaline streams can be admitted to the sulfide collection tank(s). Process controls must be diligently executed to insure, for example, that the pH of sulfide-bearing bate liquors do not drop below the optimal, slightly alkaline levels.

Because of these restrictions and due to severe limitations on available space, alternative A was eliminated from further consideration.

Under normal scheduling conditions not more than two hair-burn discharges are anticipated during any two-hour interval. The sulfide oxidation system must be capable of collecting and treating unhairing wastes from two hide processors in any two-hour interval. For a batch oxidation system, therefore, a capacity equivalent to the volume of unhairing wastes from two hide processors is required. Also, storage capacity equivalent to the volume of one hide processor's unhairing waste should be provided for collection of wastes which may be discharged out of phase during a batch sulfide oxidation run. This additional storage capacity would equal 6,300, 3,300 and 730 gallons for treatment alternatives B, C and D, respectively.

SULFIDE OXIDATION PROCESS ALTERNATIVES

In evaluating designs for the sulfide oxidation system, the criteria for aeration equipment and/or chemical treatment included energy efficiency, chemical costs, and area and volume requirements. All of the aeration systems were evaluated assuming the use of manganous sulfate as a catalyst for sulfide oxidation.

Among the proposals considered were:

1) Chemical Oxidation
2) Diffused Air Aeration
3) Submerged Turbine Aeration
4) Paddle Vat Aeration
5) Surface Aeration

Chemical Oxidation

While the oxidation of low concentrations of sulfides in water and wastes has been demonstrated to be technologically feasible using such strong oxidants as ozone, potassium permanganate, chlorine and hydrogen peroxide, the cost of such chemical treatments is prohibitive when high sulfide levels are encountered.

Potassium Permanganate--

According to Stewart (53) potassium permanganate reacts with sulfide in alkaline solution as shown below:

$$8MnO_4^- + 3S^= + 4H_2O \longrightarrow 8MnO_2 + 3SO_4^= + 8OH^-$$

The potassium permanganate-to-sulfide ratio predicted for the stoichiometric oxidation of sulfide to sulfate is 13.2 lb $KMnO_4$/lb $S^=$. At the September 1975 price of \$0.48 per pound, potassium permanganate oxidation of sulfides would cost \$6.34 per pound of sulfide.

Hydrogen Peroxide--

Operating data for hydrogen peroxide control of hydrogen sulfide at Ft. Lauderdale, Florida, and Los Angeles, California (54), indicate that hydrogen peroxide-to-sulfide ratios of 3:1 to 8.2:1 are required for elimination of sulfides in sewage mains. Using \$.33/lb hydrogen peroxide (September 1975-tankcars) costs could vary from \$.99 to \$2.70 per pound of sulfide treated.

Chlorine--

Theoretical considerations for the oxidation of sulfides using elemental chlorine indicate that a stoichiometric conversion to sulfur requires only 2.22 lb Cl_2/lb $S^=$, while a stoichiometric oxidation to sulfate requires 8.87 lb Cl_2/lb $S^=$ (55). Black & Goodson (56) showed that in dilute sulfide solutions when chlorine was offered at a 10 to 1 ratio, 4.1 parts of chlorine were consumed per part of sulfide at a pH of 8.95.

The Los Angeles County Sanitary Districts (57) estimated chlorine requirements in laboratory tests to be 3-9 lb Cl_2/lb $S^=$. In practice, however, 12 mg/l of chlorine reduced the sewage sulfide entering the treatment facility from 1.05 mg/l to 0.43 mg/l for a 19:1 ratio of Cl_2 offered-to-sulfide oxidized.

Therefore, using elemental chlorine at 5.75 cents per pound (September 1975-tankcars) chemical costs for oxidation of sulfide are postulated to be in excess of \$1.09/lb S at the 19-to-1 chlorine-to-sulfide ratio.

Ozone--

One possible reaction for the ozonation of sulfide in alkaline solution is:

$$4O_3 + S^= \rightarrow SO_4^= + 4O_2$$

The dissolved oxygen thus generated would also be available for oxidation of sulfides. However, the degree to which this secondary oxidation proceeds is not known. Maximum ozone requirements, on the basis of stoichiometry alone, are 6.0 lb O_3 per lb $S^=$.

According to Fair, Geyer and Okum (58), approximately 11.4 to 13.6 kwh of electricity are required to generate one pound of ozone from air. At 2.3¢/kwh energy would cost \$0.26 to \$0.31 per pound of ozone. On this basis, ozonation costs of approximately \$1.56 to \$1.86 per pound of sulfide are conservatively estimated. However, any sulfide oxidation by molecular O_2 which may take place will significantly reduce these costs.

With the chemical costs ranging from \$0.99 lb $S^=$ for hydrogen peroxide to \$6.34 lb $S^=$ for potassium permanganate, chemical oxidation of sulfides in unhairing waste (at a daily cost of \$1,100-\$7,040) is clearly prohibitive. It is conceivable, however, that such chemical agents could be used in a "polishing" step to provide a space efficient (but costly) alternative to the aeration of large volumes of low concentration wastes.

Diffused Air Aeration

One method of achieving oxygen transfer into wastewaters is by air diffusion. Compressed air is blown in through a network of air diffusion nozzles strategically located near the bottom of the aeration tank. By releasing the air as minute bubbles, an extremely large surface area is created to maximize oxygen transfer at the air-liquid interface. Once the oxygen requirement of the treatment process has been established, aeration requirements can be determined using the equations illustrated in Figures 24 and 25 (59).

Treatment alternative B (Table 44) calls for the batchwise oxidation of 180 pounds of sulfide contained in 12,600 gallons of waste (from two hide processors) within a two-hour interval. After deducting 30 minutes for filling and draining the reaction vessel, the time available for aeration is reduced to approximately 90 minutes, increasing the required design oxygen transfer rate to 120 lb O_2/hr. The design temperature is 30°C and the elevation is +700 ft. For a "typical" air diffusion system, (the Rexnord Air Lock Crown Diffuser)(60) the manufacturer's standard efficiency rating is 8.6% at a 13 ft submergence and 15 scfm air flow per diffuser. Thus, under actual operating conditions, the transfer efficiency for each diffuser would be 8.8%. At 15 scfm per diffuser approximately 0.255 lb O_2/min would be offered (61). Each diffuser would transfer:

$$0.255 \text{ lb } O_2/\text{min} \times 60 \text{ min/hr} \times .088 = 1.35 \text{ lb } O_2/\text{hr}$$

Therefore, 89 diffusers would be required to achieve the design transfer rate of 120 lb/hr. Since the manufacturer's recommended minimum surface requirement is one square foot per diffuser, the minimum tank area would be 89 ft^2.

Thus, a 12 ft diameter tank with a liquid depth of 15 ft (12,600 gallon capacity) plus approximately three feet of freeboard could be used. Air offered would equal 1,340 scfm at 5.85 psi and approximately 60 hp of blower capacity would be required (62).

Similarly, Treatment Alternative C would require approximately 50 hp of aeration capacity to provide 1,050 scfm of equivalent to 94 lb O_2/hr through 70 diffusion heads. The required tank diameter would be reduced to 10 ft.

Finally, Treatment Alternative D requires 30 hp of aeration capacity to provide 54 lb O_2/hr (600 scfm) through 40 diffusion heads. The tank diameter could be further reduced to eight feet.

$$Ea = Es \left[\frac{(Alt)\ (\beta)\ (Cm) - C_1}{C_{sm}}\right]\left[\alpha\right]\left[1.024^{T-20}\right]$$

where Ea = transfer efficiency of the equipment in the treatment system, %

E_s = transfer efficiency of the equipment under standard conditions, %

Alt= Altitude Correction = ratio of barometric pressure at design altitude to pressure at sea level.

C_m = mean saturation value of oxygen in tap water at the aeration mid-depth at temperature T, mg/l. (Figure 25)

C_{sm}= mean saturation value of oxygen in tap water at the aeration mid-depth at 20°C, mg/l. (Figure 25)

C_1 = dissolved oxygen operating level, mg/l.

β = ratio of oxygen saturation in waste to that in tap water at the same temperature.

α = ratio of oxygen transfer in waste to that in tap water at the same temperature.

T = temperature, °C

Given: C_1 = 0 mg/l; β =1.0; α =1.0; T=30°C; E_s=8.6%; Alt=0.975

$$Ea = 8.6\% \left[\frac{(.975)\ (1.0)\ (8.51\ mg/l) - 0\ mg/l}{10.3\ mg/l}\right]\left[(1.0)\right]\left[(1.029)^{30-20}\right]$$

$$Ea = 8.6\% \left[\frac{8.30\ mg/l}{10.3\ mg/l}\right] \times \left[1.27\right]$$

$$Ea = 8.6\% \left[(.805)\ (1.27)\right] = 8.8\%$$

Figure 24. Determination of field transfer efficiency.

$$C_{sm} = C_s \left[\frac{P_b}{29.4} + \frac{O_t}{42} \right]$$

Where C_s = O_2 saturation concentration at a given temperature in tap water, mg/l.

C_s (20°C) = 7.44 mg/l

C_s (30°C) = 9.12 mg/l

C_m = C_{sm} at 20°C

P_b = absolute pressure at the depth of air release, psi

depth of air release = 13 ft

$$P_b = 14.7 \text{ psi} + \left[\frac{62.4 \text{ lb/ft}^3}{144 \text{ in}^2\text{/ft}^2} \times 13 \text{ ft} \right] = 20.3 \text{ psi}$$

O_t = concentration of oxygen in air leaving aeration tank, %

O_t = 20.5 - (20.5 x 0.086) = 18.7%

$$C_{sm} = 9.02 \text{ mg/l} \left[\frac{20.3 \text{ psi}}{29.4 \text{ psi}} + \frac{18.7}{42} \right] = 10.3 \text{ mg/l}$$

$$C_m = 7.44 \text{ mg/l} \left[\frac{20.3 \text{ psi}}{29.4 \text{ psi}} + \frac{18.7}{42} \right] = 8.51 \text{ mg/l}$$

Figure 25. Determination of mean oxygen saturation value.

Submerged Turbine Aeration

Another common method of aeration for waste treatment is submerged turbine aeration. Like diffused air aeration, compressed air is blown into the bottom of the treatment vessel for distribution throughout the reaction medium. Unlike diffused air, however, this distribution is carried out by the sparging effect of a turbine. Air is introduced through the hollow turbine shaft into the bottom of the tank, and the turbine blades shear the air into minute bubbles which are evenly distributed throughout the tank. Given the oxygen transfer requirement for Treatment Alternative B of 120 lb O_2/hr and assuming that the ratio of field efficiencies to manufacturer-standard efficiencies is 1.02 as computed for air diffusion, aeration requirements for submerged turbine aeration can be calculated from manufacturer-standard efficiencies reported for a submerged turbine. The Eimco NS-8 submerged turbine aerators (63) are nominally rated at 3.3 lb O_2 transferred per horsepower-hour at standard conditions. Field transfer rates, therefore, of 3.4 lb O_2/hp-hr are predicted. The total power requirement estimated for the submerged turbine is 35.3 brake-horsepower. At a drive efficiency of 82%, the actual nameplate horsepower requirement would be 43.1. Therefore, a 50 hp turbine could be employed using an additional 20 hp to supply 282 scfm or air, for a total power requirement of 70 hp. With a maximum manufacturer-recommended power-to-volume ratio of five horsepower per thousand cubic feet, a tank capacity of 75,000 gallons would be required. At a liquid depth of 15' the surface dimensions of such a tank could be 30' diameter (or 26' square). For Treatment Alternatives C and D, approximately 60 and 30 hp, respectively, would be required with corresponding tank volumes of 60,000 (26' diameter) and 30,000 (18.5 ft diameter) gallons.

Paddle Vat Aeration

One viable alternative for tanners makes use of abandoned (or new) paddle vats for the aeration of sulfide-wastes. Pilot studies at Pfister & Vogel Tanning Company demonstrated a mean sulfide oxidation rate of 17 lb $S^=$/hr for 3,300 gallon batches in a 4,000 gal capacity paddle vat, using manganous sulfate as catalyst.

For Treatment Alternative B, a pair of paddle vats must be available for each 6,300 gallon process discharge.

At 34 lb $S^=$/hr (for two paddle vats) approximately 2.75 hours of aeration would be required per 6,300 gallon batch. Allowing 0.5 hour to fill and drain the two paddle vats, the total batch time would be increased to 3.25 hours for an effective rate of 27.7 lb $S^=$/hr per pair of paddle vats. Therefore, to oxidize sulfides at the design loading of 90 pounds per hour, eight paddle vats would be required (four pairs). Pfister & Vogel's paddles were fitted with 15 hp motors. While the nameplate-horsepower thus predicted equals 120, actual power requirements may be substantially lower since the paddle vats were originally designed for operation under the more strenuous conditions of processing leather. The effective volumetric requirement would be 26,000 gallons with a net surface area of approximately 1,000 ft^2.

For Treatment Alternative C, five paddle vats would be needed with a total effective capacity of 16,000 gallons and 630 ft^2 of surface area. Likewise, the requirements for Treatment Alternative D include 3 paddle vats with an effective total volume of 10,000 gallons having 380 ft^2 of surface area.

Thus, while paddle aeration can reduce capital expenditures when abandoned or under-utilized equipment is available, power costs are relatively high and a great deal of manufacturing floor space must be sacrificed.

Surface Aeration

Another type of aeration applicable to the manganese-catalyzed air oxidation of sulfides in unhairing wastes is surface aeration. In contrast to air diffusion and air dispersion, surface aeration effects oxygen transfer by pumping large volumes of treatment liquor radially into the atmosphere to form a high velocity spray pattern. The droplets thus formed drastically increase the air-liquid interfacial area which is essential for oxygen transfer. Also, impingement of the spray on the liquid surface causes additional agitation, further aiding oxygenation as well as establishing a dynamic mixing pattern.

The design aerator efficiency for Alternative B was previously established at Pfister & Vogel in pilot studies utilizing a two horsepower "Aqua-Jet" (64) floating surface aerator with a manufacturer oxygen transfer rating of 3.9 lb O_2/hp-hr. At a mean, initial sulfide concentration of 1,730 mg/l, an aerator-sulfide oxidation efficiency of 7.3 lb $S^=$/hp-hr has been established for this aerator. Assuming that the sulfide oxidation efficiency-to-oxygen transfer efficiency ratio of 1.87:1 remains constant for all size "Aqua-Jet" aerators, the 20 hp "Aqua-Jet Mark 20" (oxygen transfer efficiency = 3.2 lb O_2/hp-hr) would be capable of oxidizing sulfides at the rate of 6.0 lb/hp-hr. Allowing 30 minutes to fill and empty the reaction vessel, 20 hp in aeration capacity would be required to achieve the 120 lb $S^=$/hr design rate. Aeration tank capacity should equal 13,600 gallons, incorporating the maximum surface area practicable within the limit of the minimum manufacturer recommended liquid depth of four feet.

Such a tank would have a diameter of 23 feet with a total sidewall of 7 feet including approximately 3 feet of freeboard. This design fully accommodates the 20 foot diameter impingement pattern exhibited by this aerator. Where ample floor space is unavailable, however, a reduction in design surface area is advisable as long as aerator performance is not seriously impaired. An alternative reaction vessel design, therefore, would be a 15 foot diameter tank with a liquid depth of 9.5 feet (effective volume 12,600 gallons) plus an additional 3 feet of freeboard. Likewise, a square surfaced tank could be employed having the advantage of more efficient space utilization with an increased surface-to-volume ratio. Such a design, however, would risk the development of static zones in the corners where sulfide oxidation might be inhibited due to inadequate mixing.

Finally, it is possible to install two aeration vessels, each having half of the design aeration capacity. The switch from a single 20 hp aerator to two 10 hp aerators has several practical advantages. First, in the case of the Aqua-Jet aerators, the efficiency of the 10 hp aerator is slightly higher (3.4 lb O_2/hp-hr vs 3.2 lb O_2/hp-hr) than that of the larger aerator, so that a combined sulfide oxidation rate of 128 lb $S^=$/hr (vs 120 lb/hr for a 20 hp aerator) is anticipated. Second, the installation of parallel aeration systems vastly improves operational and maintenance flexibility. Also, such a "dual-reactor" system provides the capability of comparative testing under controlled conditions.

At an aerator efficiency of 6.55 lb $S^=$/hp-hr (1.87 lb $S^=/O_2$ x 3.5 lb O_2/hp-hr for a 15 hp Aqua-Jet aerator), the requirements for Treatment Alternative C would equal 14.4 hp at the design oxidation rate of 94 lb $S^=$/hr. Thus, a 15 hp aerator would be chosen along with an aeration vessel having a 6,000 gallon capacity such as a 15 ft diameter cylindrical tank with a liquid level of 5 ft and an additional 3 ft of freeboard.

Finally, for Treatment Alternative D a sharply lower design efficiency of 3.9 lb $S^=$/hp-hr must be used. Pilot studies indicated that for the 2 hp aerator concentrated hair-burn liquors were oxidized at a rate of 4.2 lb $S^=$/hp-hr for a sulfide oxidation efficiency-to-oxygen transfer efficiency ratio of 1.08 lb $S^=$/lb O_2. At the manufacturer-oxygen transfer rate for the Aqua-Jet Mark 15 aerator of 3.5 lb O_2/hp-hr, a sulfide oxidation rate of 3.9 lb $S^=$/hp-hr is predicted. The aeration capacity required, therefore, to achieve the design sulfide oxidation rate of 54 lb $S^=$/hr is 13.9 hp. Thus, a 15 hp aerator would be specified. A reaction vessel with an 8,000 gallon capacity (15' diameter x 6'-1" deep plus 3' of freeboard) capable of containing a full day's loading would be recommended. Anticipated operation of this system would incorporate batchwise aeration over a 90 minute interval with a subsequent partial draw-off of treated effluent to accommodate fresh wastes.

The data in Table 45 illustrates various chemical oxidation procedures with operating costs of \$0.99 to \$0.34 per pound of sulfide to be 21 to 135 times as costly as the most expensive aeration alternative. Removing 1,000 lb $S^=$/day by the least expensive chemical oxidation alternative would cost more than \$250,000 annually. The operating costs projected for every aeration alternative considered are drastically lower than for chemical treatment.

Catalyst costs for each of the aeration alternatives were computed on the basis of catalyst-to-sulfide ratios employed in the Paddle Vat aeration studies. The optimum was shown to lie within the 0.10-0.15 $Mn^{++}/S^=$ range for manganous sulfate. A ratio of 0.15 was therefore chosen as a conservative value for this feasibility study.

The pilot aeration studies show that "spent" catalyst retains much of its activity and reuse of the "manganese hydroxide" sludge is expected to greatly reduce catalyst requirements. It appears from Table 45 that catalyst cost-to-power cost ratios would range from 1.7:1 to 13:1. In practice, however, it is anticipated that these ratios could be substantially lower with catalyst optimization.

It was assumed that the optimum catalyst dosage for the manganese

TABLE 45. OPERATING COSTS FOR VARIOUS SULFIDE OXIDATION METHODS

Alternative	Process	Volume, gal per hide processor	Tank area, ft^2	Power, kwh/lb $S^=$	Operating cost ($/lb $S^=$) Power	Chemical	Total**
B	Air Diffusion	6,300	113	0.33	0.0087	0.0295	0.0382
B	Air Dispersion	6,300	707	0.44	0.0101	0.0295	0.0396
B	Paddle Aeration	6,300	1,010	0.75	0.0173	0.0295	0.0468
B	Surface Aeration	6,300	177	0.12	0.0028	0.0295	0.0323
B	Chemical Oxidation	3,300	-	11.4 -* 13.6	0.262 - 0.313	0.99-6.34	0.99-6.34
C	Air Diffusion	3,300	79	0.40	0.0092	0.0295	0.0387
C	Air Dispersion	3,300	531	0.48	0.0111	0.0295	0.0406
C	Paddle Aeration	3,300	630	0.60	0.0134	0.0295	0.0423
C	Surface Aeration	3,300	177	0.10	0.0023	0.0295	0.0318
C	Chemical Oxidation	3,300	-	11.4 -* 13.6	0.262 - 0.313	0.99-6.34	0.99-6.34
D	Air Diffusion	730	50	0.42	0.0097	0.0295	0.0392
D	Air Dispersion	730	278	0.42	0.0097	0.0295	0.0392
D	Paddle Aeration	730	378	0.55	0.0126	0.0295	0.0421
D	Surface Aeration	730	177	0.21	0.0048	0.0295	0.0343
D	Chemical Oxidation	730	-	11.4 -* 13.6	0.262 - 0.313	0.99-6.34	0.99-6.34

* Ozone only.

** excluding labor pumping and maintenance costs.

catalyzed air oxidation of sulfides would be the same for each of the aeration alternatives. Power requirements and surface requirements were weighted most heavily since it is impossible to predict the real differences in catalyst requirement attributable to the various types of aeration. Further, it is assumed that present trends in the cost and availability of electric power will continue, so that the importance of power costs relative to catalyst costs will continue to increase.

Surface aeration was chosen as the preferred system for aeration of sulfide-bearing wastes for all three treatment levels primarily because of the much lower power requirements vs alternate aeration systems.

Even though area requirements were substantially greater than those for air diffusion, the 177 ft^2 required for surface aeration was well within the strictures of available plant area.

Further consideration was given to the desirability of a dual-reactor capability in the sulfide oxidation system design. Two ten-horsepower floating surface aerators and two 12 ft diameter reaction vessels were incorporated in a modified design for Treatment Alternative C.

Ample aeration capacity was included so that at a future date, by installing a 6,600 gallon storage tank, the sulfide oxidation system could be converted to meet the requirements of Treatment Alternative B.

Two 12 ft diameter by 11 ft deep fiberglass reinforced resin tanks were installed, taking advantage of the extra head space offered by sinking them into existing paddle pits and incorporating existing sewers. The resin used in construction of the tanks was specified for use under both pH extremes.

The aerators were designed in stainless steel to withstand the harsh chemical environment as well as the turbulent hydraulics envisioned. A three ft high stainless steel cylindrical motor shield with a one-way condensate drain was specified to protect the aerator motors from inundation by foam. Each aerator was moored using three guide posts installed vertically at the corners of an equilateral triangle within the aeration tanks and three slide rings welded to the circumference of the aerator floats.

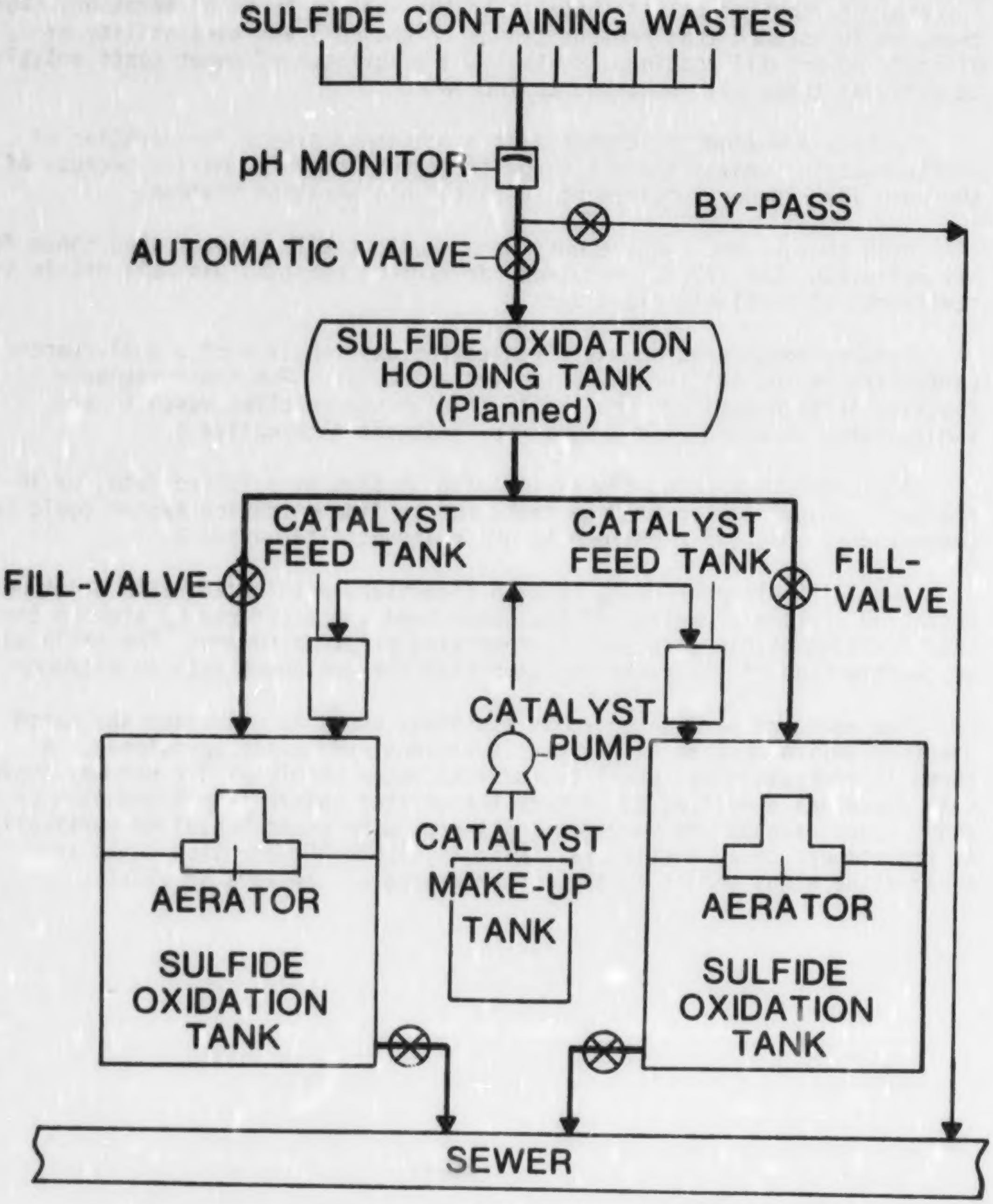
SULFIDE CONTAINING WASTES
pH MONITOR
BY-PASS
AUTOMATIC VALVE
SULFIDE OXIDATION HOLDING TANK (Planned)
CATALYST FEED TANK
CATALYST FEED TANK
FILL-VALVE
FILL-VALVE
CATALYST PUMP
CATALYST MAKE-UP TANK
AERATOR
SULFIDE OXIDATION TANK
AERATOR
SULFIDE OXIDATION TANK
SEWER

Figure 26: SULFIDE OXIDATION SYSTEM.

SECTION XIII

SULFIDE OXIDATION SYSTEM-FULL-SCALE OPERATION

The full-scale Sulfide Oxidation System, as illustrated in Figure 26, incorporates two ten-horsepower, floating surface aerators in separate 7,000 gallon capacity cylindrical reaction tanks. Each tank measures 12 ft in diameter with an 11 ft sidewall. At the 7,000 gallon level, 2.75 ft of freeboard is provided. A valve manifold at the end of the "hairburn header" pipe allows the operator to direct sulfide wastes to either of the reaction tanks or to bypass them to the sewer. A continuous in-line pH monitor is located in the hairburn header with a low-level alarm relay set at pH 10.0. If the pH in the header drops below the alarm level an automatic air-operated valve closes and an alarm sounds. Since this automatic valve is upstream of the two reaction tank fill-valves (but downstream from the bypass valve) acidic wastes cannot be admitted to the sulfide oxidation system.

A 400 gallon fiberglass tank with a high speed chemical mixer has been installed for catalyst make-up. A standard (1 lb Mn^{++}/gal) solution of manganous sulfate is prepared daily and pumped to graduated, 30 gallon capacity, gravity feed tanks for batch-wise addition to the aeration tanks as required. Aerators are moored to guide posts within the aeration tanks so that they can operate at liquid levels from 3 to 9 feet. Adequate space has been provided overhead for the future installation of a 6,600 gallon holding tank to increase treatment capabilities.

Full-scale operating data confirm pilot study results for the manganese catalyzed air oxidation of sulfides in unhairing wastes and for the scale-up of surface aeration equipment. For ten oxidation runs at catalyst-to-sulfide dosages varying from 0.05 to 0.15 lb Mn^{++}/lb $S^{=}$, a mean time of 2.75 hours was required to oxidize the sulfide in 6,400 gallons of unhairing waste from 2,830 mg/l to zero. The rate of oxidation over the ten runs averaged 58.3 lb $S^{=}$/hr for an average aerator efficiency of 5.83 lb $S^{=}$/hp-hr.

The time required for 98% reduction of the sulfide, however, is only 2.125 hours per sulfide oxidation run for an efficiency of 6.89 lb $S^{=}$/hp-hr. Thus, while the rate observed for oxidation to the zero sulfide level is within 91% of the design efficiency of 6.4 lb $S^{=}$/hp-hr, the mean rate observed for 98% removal of sulfide actually exceeds the design rate. The maximum incremental efficiency observed during full-scale operation was 15.2 lb $S^{=}$/hp-hr. However, during the "die-off phase" of the reaction where the last two percent of the sulfide is oxidized the efficiency is reduced to a mere 0.5 lb $S^{=}$/hp-hr.

OPTIMUM CATALYST-TO-SULFIDE RATIO

To determine the effect of catalyst dosage during the full-scale oxidation of sulfides from unhairing wastes in a surface aeration system, varying amounts of manganous sulfate monohydrate (Carus Mn28) were added in three liquid feeds 30 minutes apart to approximately 6,000-7,000 gallon batches of unhairing wastes. The unhairing wastes for each aeration run were composed of concentrated hair-burn liquor and approximately half of the subsequent wash from two hide processor production runs. Initial sulfide concentrations varied from 2,310 mg/l to 3,600 mg/l with the total initial sulfide content of the batches varying from 117 lb to 175 lb. Initial temperatures averaged approximately 34°F, while finals were approximately 10° higher. Following each run the aeration tank was drained and hosed with fresh water to remove all residual catalyst-sludge.

The data in Table 46 illustrate that a baseline sulfide oxidation run without any catalyst required nine hours of aeration to reduce the initial sulfide concentration from 2,720 mg/l (148 lb) to 65 mg/l (3.5 lb), for a treatment efficiency of 97.6%. The mean oxidation rate was 16.1 lb $S^=$/hr. The corresponding mean and maximum sulfide oxidation-aerator efficiencies were 1.61 lb $S^=$/hp-hr and 2.55 lb $S^=$/hp-hr, respectively.

When manganous sulfate was added at a 0.025 $Mn^{++}/S^=$ ratio in a subsequent run, the oxidation rate was substantially improved, with only 5.5 hours of aeration required to reduce the sulfide from an initial concentration of 2,310 mg/l (117 lb) to a "zero detectable" level. The mean rate of 21.3 lb $S^=$/hr was 32% greater than the no-catalyst rate, while the maximum 15 minute-incremental rate soared to 87.2 lb $S^=$/hr, nearly 3.5 times the "un-catalyzed" maximum.

Likewise, by increasing the catalyst-to-initial sulfide ratio to 0.0375 a marked improvement in the mean oxidation rate to 31.8 lb $S^=$/hr was effected. The time required to achieve a zero sulfide level was further decreased to 4.5 hours but a decrease in the maximum 15 minute-incremental rate to 70.7 lb $S^=$/hr was also observed.

A further increase in catalyst levels demonstrated improved oxidation rates in three separate runs at the 0.05 $Mn^{++}/S^=$ ratio. For these three runs initial sulfides averaged 3,110 mg/l (157 lb) requiring slightly more than 2.75 hours of aeration to reach the zero sulfide level. The mean rate of oxidation for the three runs was 55.5 lb $S^=$/hr, while the maximum 15 minute-incremental rate recorded was 152 lb $S^=$/hr.

A sulfide oxidation run at the 0.10 $Mn^{++}/S^=$ ratio required 2 hours of aeration to reduce the initial sulfide concentration of 2,660 mg/l to zero for a mean rate of 65.5 lb $S^=$/hr. The maximum incremental rate of 132 lb $S^=$/hr was slightly lower than that observed at the 0.05 catalyst-to-sulfide ratio, but higher than for the 0.0375 ratio.

Finally, five runs at the 0.15 $Mn^{++}/S^=$ ratio demonstrated that this level was clearly beyond the range of efficient catalyst utilization.

TABLE 46. EFFECT OF CATALYST DOSAGE ON SULFIDE OXIDATION

$Mn^{++}/S^{=}$	No. of trials	Volume, gal	Initial Sulfide		Time hr	Rate	
			mg/l	lb		Mean, lb $S^{=}$/hr	Maximum incremental, lb $S^{=}$/hr
0	1	6,520	2,720	148	9.0**	16.1	25.5
0.025	1	6,100	2,310	117	5.5	21.3	87.2
0.037	1	6,800	2,520	143	4.5	31.8	70.7
0.050	3	6,070*	3,110*	157*	2.83*	55.5*	152
0.100	1	5,920	2,660	131	2.0	65.5	132
0.150	5	6,710*	2,780*	155*	2.65*	58.5*	134

* Average Values

** Sulfide reduced to 65 mg/l in 9 hours

An average of approximately 2.67 hours was required to oxidize sulfides from a mean initial level of 2,780 mg/l to zero for a mean rate of oxidation over the five runs of 58.5 lb $S^=$/hr. Individual mean rates varied from 51.0 lb $S^=$/hr to 75.0 lb $S^=$/hr, while the maximum 15 minute-incremental rate observed during the five runs was 134 lb $S^=$/hr.

A mean rate of sulfide oxidation of 65.5 lb/hr was observed at the 0.10 $Mn^{++}/S^=$ ratio. The apparent increase over rates at the 0.05 and 0.15 levels, however, cannot be considered to be statistically significant since only one run was conducted at this catalyst level. Further analysis of the data (Two Sample Ranks Test: $n_1=3$, $n_2=5$, sum of ranks of smaller group = 13) indicates that the average of the mean rates for sulfide oxidation at the 0.05 and 0.15 $Mn^{++}/S^=$ ratio do not differ significantly. Therefore, it might be concluded that the optimum $Mn^{++}/S^=$ ratio for the oxidation of sulfides in unhairing wastes by surface aeration lies within the 0.05 to 0.15 range. Further investigation of these catalyst ratios is indicated, with particular attention to cost-efficiency evaluations.

These full-scale sulfide oxidation runs confirmed the observations made during previous pilot-scale oxidation runs. The color of the reaction mixture followed the same pattern, with the initial dark brown color of the unhairing waste-catalyst mixture gradually lightening to a celery green, and finally turning to beige near the zero sulfide endpoint.

Foaming also followed the trend observed in pilot runs. With approximately three feet of freeboard available, however, and due to the special aerator motor shields incorporated into the aeration system design, antifoam was not required to contain the mixture within the reaction vessel. A pronounced increase in foam generation was generally observed after approximately half of the sulfide had been oxidized and following the observed incremental rate maxima. Near the endpoint of the oxidation the foam became extremely stable and in a few cases completely concealed the aerator spray.

Consistent with the pilot studies observations, the phenomenon of regeneration of sulfides following aeration was also observed in the full-scale sulfide oxidation runs. In one run at the 0.15 catalyst-to-sulfide ratio, aeration was halted as soon as the zero detectable sulfide level was reached. After 24 hours, the aerator was turned on briefly to mix the contents of the tank and a sample was withdrawn. This sample analyzed at 123 mg/l of sulfide.

In another run the tank was sampled 3, 5 and 24 hours after the aerator was turned off, but without mixing the contents. These samples taken at a level halfway down the side of the tank analyzed at 18, 16 and 27 mg/l of sulfide, respectively. A sample of scum collected from the surface after 4 days of settling contained 12 mg/l. At the same time, an interlayer sample analyzed at 36 mg/l of sulfide while the bottom sediments contained 288 mg/l, suggesting that the regeneration phenomenon may be due to the formation of a settable, metastable precipitate which later reverts to sulfide.

Tanners must be cautioned, therefore, that treatment of sulfide-bearing wastes to a zero sulfide level does not insure the absence of sulfide from the final effluent. Rather, where appreciable storage or lagooning of "de-sulfided" wastes prior to discharge is necessary, measurable quantities of sulfide may reappear.

Another observation consistent with the pilot aeration studies indicates a slight increase in pH (approximately 0.2-0.4 pH units) which occurs during the maximum rate intervals. This sudden pH increase supports the hypothesis that sulfide is being converted to elemental sulfur according to the equation:

$$2HS^- + O_2 + 2H^+ \longrightarrow 2\,H_2O + 2S$$

The oxidation of sulfides to sulfate can be expressed as:

$$HS^- + 2O_2 \longrightarrow SO_4^= + H^+$$

or

$$HS^- + 2O_2 + OH^- \longrightarrow SO_4^= + H_2O$$

The consumption of hydroxyl ions precludes the occurrence of sulfate as the principal oxidation product.

The sulfide oxidation curve for a typical full-scale aeration run which is shown in Figure 27 very closely follows the shape of the sulfide oxidation curve (Figure 22) generated for paddle aeration. This curve may be characterized by an initial sharp decrease in sulfide concentration with decreasing slope. At a point corresponding to approximately half the initial sulfide concentration an inflection occurs followed by a phase of rapid increase in slope.

The significance of the inflection point can be emphasized by double differentiating the sulfide oxidation curve. The second differential corresponds to a plot of $\Delta S^=/\Delta T$ vs T. This rate curve (Figure 28) emphatically shows the rate maxima corresponding to 40.0 mg/l-min for this run (152 lb $S^=$/hr). With further aeration the rate of sulfide disappearance declines and approaches zero.

CATALYST VARIATIONS

The effect of potassium permanganate on the oxidation of sulfides in unhairing wastes by surface aeration was investigated in a full-scale aeration run. A 6,700 gallon batch of unhairing waste containing 2,270 mg/l of sulfide was treated with three feeds of potassium permanganate (18.7 lb $KMnO_4$) 30 minutes apart to bring the $Mn^{++}/S^=$ ratio to the 0.05 level. Initial and final temperatures of 85° and 92°F were respectively recorded. After 2.75 hours of aeration a zero sulfide reading was recorded for a mean rate of sulfide oxidation of 45.5 lb $S^=$/hr. The maximum incremental rate observed was 82.1 lb $S^=$/hr.

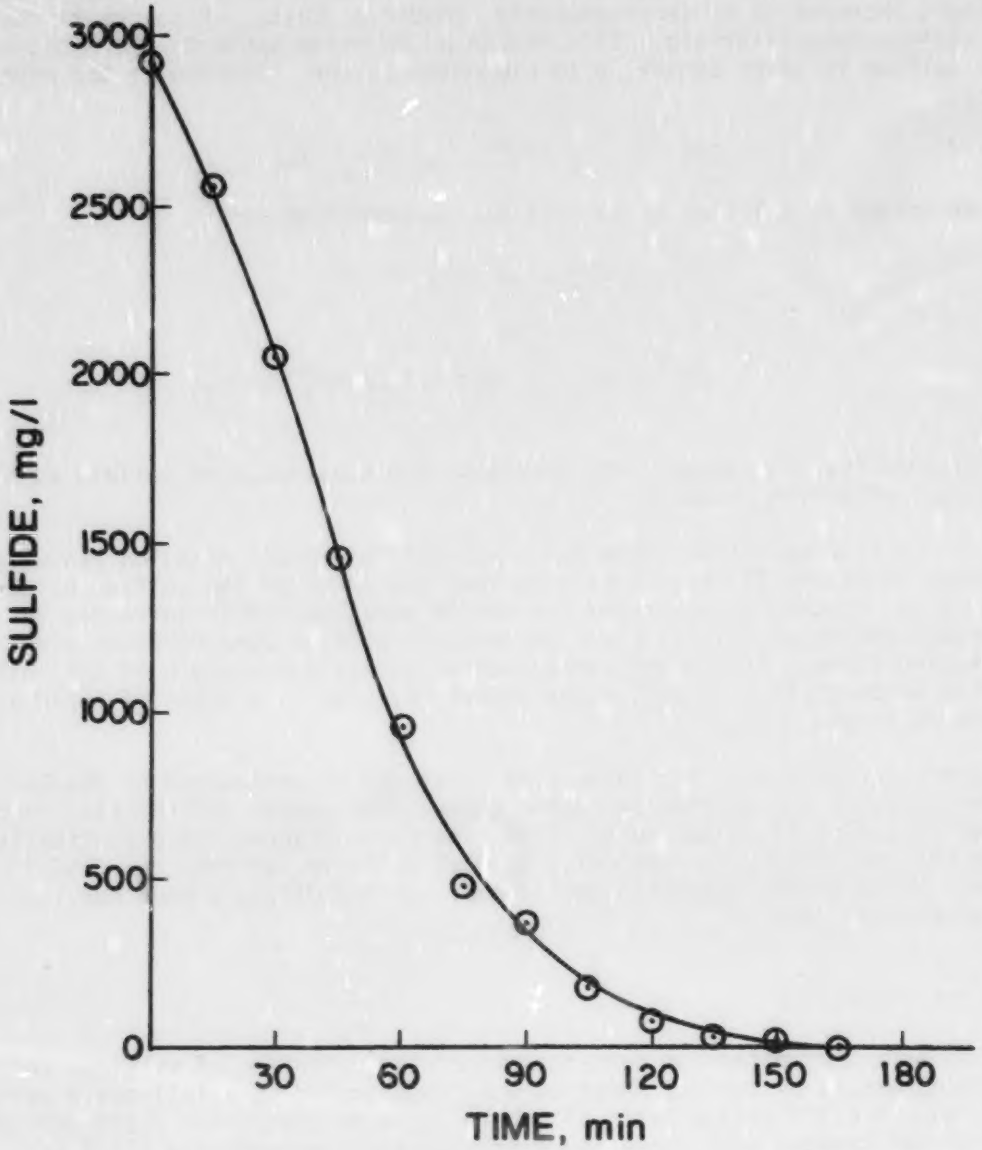

Figure 27: FULL-SCALE SULFIDE OXIDATION CURVE.

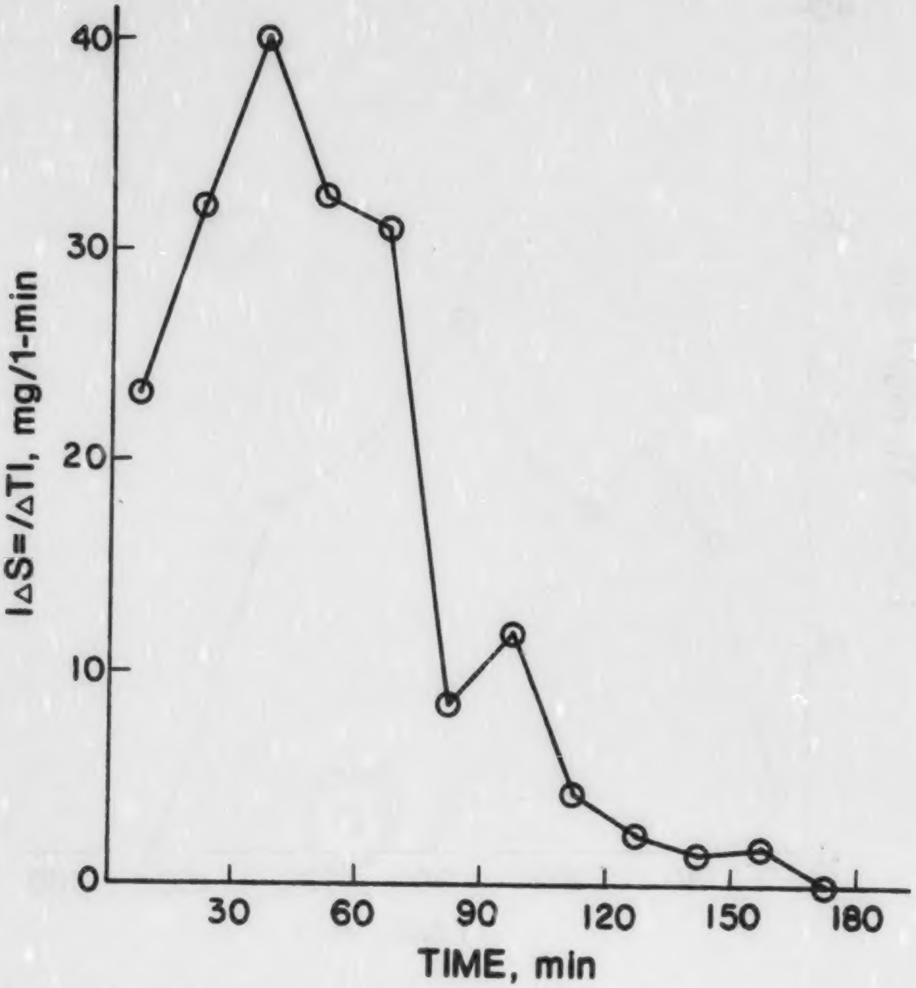

Figure 28: RATE CURVE FOR FULL-SCALE SULFIDE OXIDATION.

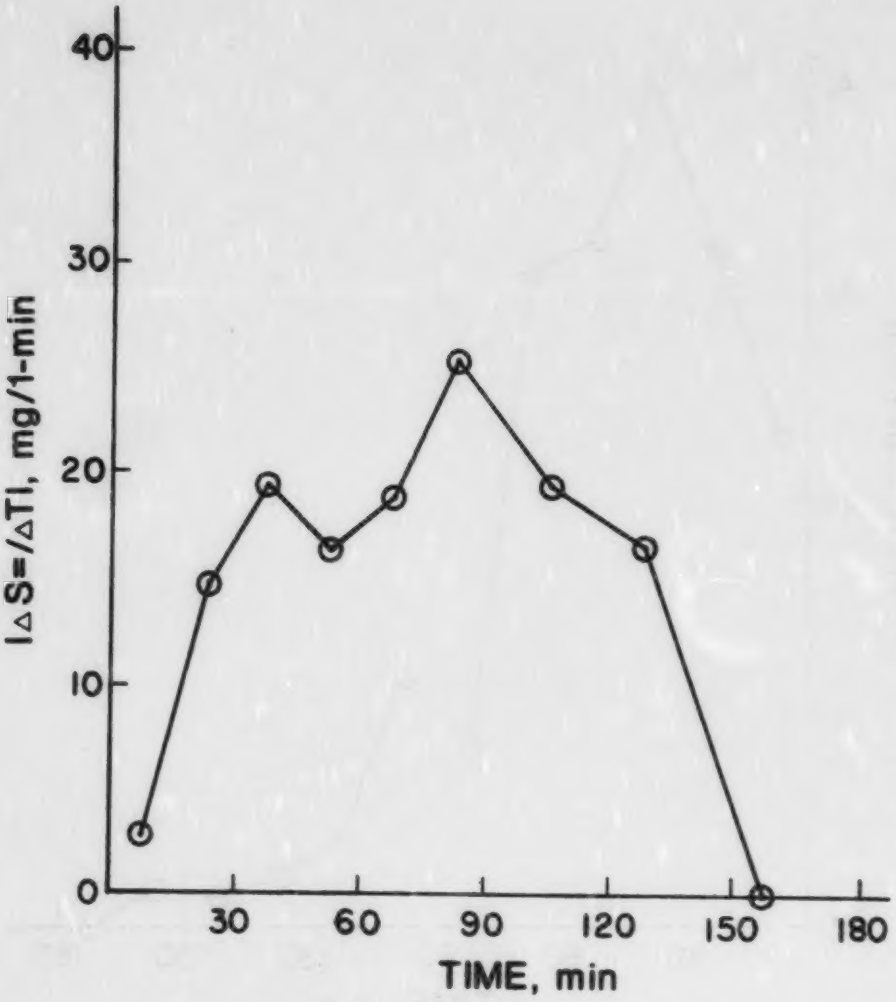

Figure 29: FULL-SCALE SULFIDE OXIDATION RATE CURVE-POTASSIUM PERMANGANATE CATALYST.

The sulfide oxidation rate curve shown in Figure 29 closely resembles the curves for full-scale aeration using manganous sulfate as catalyst. The shape of this curve, however, with the rate maximum appearing between 75 minutes and 90 minutes, sharply contrasts the earlier results for paddle aeration using potassium permanganate ($Mn^{++}/S^{=} = 0.15$), where the maximum incremental rate was observed within the first 15 minutes of the reaction. Since the cost of using potassium permanganate is approximately seven times that of manganous sulfate at equivalent $Mn^{++}/S^{=}$ ratios, and since no rate improvement was demonstrated at equal $Mn^{++}/S^{=}$ ratios, it is concluded that manganous sulfate catalysis is more cost effective than potassium permanganate for the oxidation of sulfides in unhairing wastes.

One possible explanation for the sharp contrast between the rate curves for the two aeration systems lies in the fact that in paddles, potassium permanganate was employed at a 0.15 $Mn^{++}/S^{=}$ ratio (in a single feed), three times the level employed in the full-scale oxidation run. It is possible, therefore, that in paddle aeration the activation energy for direct chemical oxidation of sulfide by permanganate was immediately surpassed, causing the early rate surge, while permanganate levels in the full-scale system were insufficient.

Also, with a manganese sulfate catalyzed air oxidation rate of roughly three times that encountered in paddle aeration, the relative contribution of air oxidation vs permanganate oxidation to the overall oxidation rate is much greater in the full-scale system. Thus, the paddle aeration results closely follow a potassium permanganate-oxidation model while the full-scale permanganate run is more closely described by a manganese catalyzed air oxidation model.

Another variation in catalyst usage was investigated in which a total $Mn^{++}/S^{=}$ ratio of 0.15 was achieved by addition of manganous sulfate in eleven liquid feeds, 15 minutes apart. The first feed, at time zero, was made at a $Mn^{++}/S^{=}$ ratio of 0.05. At successive 15 minute intervals additional feeds were made to increase the $Mn^{++}/S^{=}$ ratio in 0.01 increments to a final level of 0.15. Two and one-half hours of aeration were required to reduce the sulfide in approximately 6,500 gallons of waste from an initial concentration of 2,480 mg/l to zero. The mean rate of oxidation was 53.7 lb $S^{=}$/hr, while the maximum incremental rate observed was 112 lb $S^{=}$/hr, neither of which shows an improvement over previous runs at the 0.05, 0.10 and 0.15 $Mn^{++}/S^{=}$ ratios where catalyst was added in three liquid feeds 30 minutes apart.

AGED UNHAIRING WASTES

To determine the effect of the aging of unhairing wastes on the manganese catalyzed air oxidation of sulfides, approximately 7,000 gallons of unhairing wastes were stored at ambient temperature for twelve days, and were subsequently treated by surface aeration. After aging, the waste analyzed at 2,930 mg/l of sulfide and the temperature was 84°F. Manganous sulfate was added in three liquid feeds 30 minutes apart to a $Mn^{++}/S^{=}$ ratio of 0.15. After 9.5 hours of aeration a zero sulfide reading was established. The mean rate of oxidation was thus reduced to 37.6 lb $S^=$/hr, while the maximum incremental rate was 66.0 lb $S^=$/hr. This maximum occurred at a much lower sulfide concentration than for fresh unhairing waste.

In a subsequent sulfide oxidation run with two month old unhairing waste, six hours of aeration was required to reduce the sulfide level from 3,040 mg/l to 145 mg/l. Thus, the mean rate of oxidation dropped further to 25.2 lb $S^=$/hr. The maximum incremental rate observed, however, increased markedly over the previous run to 144 lb $S^=$/hr. Also, in contrast to the earlier run, this maximum incremental rate was observed early in the reaction (15 minutes to 30 minutes) reducing the sulfide concentration from 2,880 mg/l to 2,190 mg/l within a 15 minute interval. The pH of the reaction mixture increased from 11.48 to 11.89 over the 6 hour period, with most of the increase occurring during the maximum rate interval.

Thus, it is obvious that the extended aging of unhairing wastes prior to aeration seriously reduces the mean sulfide oxidation efficiency of this manganese-catalyzed surface aeration system.

FOAMING

During these full-scale sulfide oxidations two runs were atypical with respect to severity of foaming. In both runs during the second half of the reaction, the foam layers were extremely stable measuring approximately 2.5 to 3 feet in thickness. The resultant reduction in mixing efficiency caused a stratification to occur within the reaction vessel.

To approximately 6,000 gallons of unhairing wastes containing 2,580 mg/l of sulfide, manganous sulfate catalyst was added in three liquid feeds at 30 minute intervals for a $Mn^{++}/S^=$ ratio of 0.15. Only two hours of aeration was required to reduce the sulfide level to 45 mg/l. Thus, a sulfide removal efficiency of better than 98% was achieved at a mean rate of 61.0 lb $S^=$/hr. At this point, foaming was so severe that the aerator spray was completely concealed and the foam layer was within 6 inches of the top of the motor shield (three feet high). The reaction very closely followed the pattern established by previous runs except that even with an additional three hours of aeration the zero sulfide level could not be attained. After a total of five hours of aeration, a grab sample taken approximately halfway down the side of the reaction vessel analyzed at 4 mg/l $S^=$. Another sample, however, taken from the bottom of the tank revealed a sludge layer which contained 54 mg/l of sulfide.

Another run using 5,500 gallons of unhairing waste showed similar results at the 0.05 $Mn^{++}/S^=$ ratio. Again, unusually severe foaming was observed during the declining-rate phase of the reaction. Only two hours of aeration was required for a 98% reduction in the sulfide concentration from an initial level of 2,590 mg/l. With another 2.5 hours of aeration, however, the sulfide level could only be reduced to 13 mg/l.

While the cause of this foaming remains undetermined, it is possible to achieve partial control over foaming. In a subsequent oxidation run, silicone antifoam was added during the declining-rate phase of the reaction. Approximately 7,000 gallons of unhairing waste containing 2,740 mg/l of sulfide was aerated for 1.5 hours ($Mn^{++}/S^{=}$ = 0.15) to reduce the sulfide to 290 mg/l. A 1% solution of silicone antifoam was continuously added over the next 1.5 hour interval. The antifoam partially restrained foaming so that the aerator spray could just be observed. After a total of 3.0 hours of aeration, a sample which was representative of the entire reaction vessel contents contained no sulfide. The mean rate of oxidation was 51 lb $S^{=}$/hr with a maximum incremental rate of 101.6 lb $S^{=}$/hr.

Approximately 5.5 pounds of silicone antifoam was required to control the foaming. At a price of $1.40 per pound for the antifoam, the cost to control foaming would be $7.70 per sulfide oxidation run. Since this antifoam improves sulfide removal efficiency for only the last two percent of sulfide (approximately 3 pounds), the cost per pound of sulfide is approximately $2.50. Thus, while such antifoams are capable of controlling foaming and thus completing the oxidation, auxiliary mixing by air injection, fluid recirculation into the bottom of the reaction vessel, or an aerator draft tube should be investigated as more economically-acceptable ways of achieving the zero sulfide endpoint.

TEMPERATURE

To determine the effect of temperature on the rate of sulfide oxidation, aeration runs were conducted using unhairing wastes at 98°F and 72°F (the normal temperature before sulfide oxidation is 82°-86°F).

For the high-temperature run, approximately 5,000 gallons of unhairing wastes from two hide processor runs were collected in the 7,000 gallon capacity reactor vessel and diluted with clean hot water to the 6,500 gallon level. The temperature after dilution was 98°F and the sulfides analyzed at 2,640 mg/l. Manganous sulfate catalyst was added in three liquid feeds for a 0.05 $Mn^{++}/S^{=}$ ratio. After 3.75 hours of aeration, a zero sulfide level was achieved. Thus, a mean oxidation rate of 38.2 lb $S^{=}$/hr was observed, well below the 51.7 to 58.4 lb $S^{=}$/hr previously observed at this catalyst level. The maximum incremental rate was 66.2 lb $S^{=}$/hr and the final temperature was 99°F.

In the low temperature run, 5,000 gallons of waste were diluted to 6,500 gallons with clean, cold water to give an initial sulfide concentration of 2,290 mg/l. With three hours of aeration required to reduce the sulfide concentration to zero, the mean rate of oxidation was 40.7 lb $S^{=}$/hr. The maximum incremental rate observed as 85.7 lb $S^{=}$/hr and the final reaction temperature was recorded at 79°F.

In both runs two liters (approximately 4.5 pounds) of a silicone antifoam, Dow Corning DB-31, were added when foaming became severe. A 1% solution of the antifoam was dribbled into the spray pattern to help control foam and insure adequate mixing.

The lower-than-normal rate observed in the low temperature run is consistent with the basic rules of thermodynamics. The reduced rate at elevated temperatures, however, is contrary to the expected results. The reason for this lower rate may, in part, be the reduced solubility of oxygen at elevated temperatures. Also, as the limited one degree fahrenheit temperature increase suggests, the heat of reaction (which normally produces a temperature increase of approximately 10°F) was probably dissipated to the ambient air as water vapor. Turbulence at the surface of the reaction vessel increases the surface area for evaporation to take place. This steam could generate convection currents carrying fresh air away from the liquid surface. Thus, an "oxygen starvation" condition may exist at the elevated temperature. It may be possible to correct this "oxygen starvation" by installing a small fan to blow fresh cool air over the surface of the reaction vessel.

Therefore, as these experiments indicate, the normal starting temperature of 82-84°F is probably close to the optimum for the batch-wise manganese catalyzed air oxidation of sulfides in unhairing wastes for this system.

AERATOR MOORING

One mechanical problem encountered during these oxidation runs was the tipping of the floating surface aerator during aeration. This tipping appears to be related to wastewater foaming, and is most pronounced during the declining-rate phase of the sulfide oxidation reaction. Also, heavy doses of antifoam added to reduce foaming rapidly improves the condition. Although, after consultation with the manufacturer's technical representatives, the exact cause of the aerator tipping remains unknown, it may be related to an increase in buoyancy and a shifting of the center of gravity relative to the liquid surface. While it appears that this tipping had no effect on the efficiency of sulfide oxidation, it is unacceptable from an operations standpoint. When the aerator tips approximately 30° from vertical, the float "jams" within the aerator guide posts. Subsequent emptying of the reaction vessel leaves the aerator precariously suspended, and upon release serious damage could occur.

In one attempt to correct aerator tipping, a 400 pound (100 pounds had no effect on tipping) counterweight was attached to the aerator motor housing. This counterweight which equalled almost half the installed weight of the aerator, maintained the aerator in a nearly level position throughout one oxidation run. Observation of the spray pattern revealed a below-normal pumping rate. The 6,000 gallon-batch of unhairing waste required 4 hours of aeration to reduce the sulfide from an initial level of 3,970 mg/l to 531 mg/l for an average oxidation rate of 41.8 lb $S^{=}$/hr ($Mn^{++}/S^{=} = 0.05$). After 8 hours of aeration, a sample of waste taken near the surface contained 50 mg/l of sulfide, while a sample from the bottom still contained 3,330 mg/l, indicating that the mixing pattern was indeed very poor, corroborating the low pumping rate observation.

In subsequent aeration runs, three guy lines were connected from the top of the motor housing to the edge of the oxidation tank. By maintaining equal tension on these lines, the aerator remained level throughout the oxidation run. Thus, another alternative to the present mooring system would be to use a set of three or more spring-loaded or counterbalanced mooring cables fixed to the sidewall of the reaction vessel. Such a mooring system would provide horizontal stability while allowing the aerator to float on the surface at any level within operating limits.

SEQUENTIAL OXIDATION

To test the hypothesis that the manganese floc-substrate in the sulfide oxidation process retains its catalytic activity when reused in subsequent sulfide oxidation runs, approximately 3,300 gallons of unhairing waste were aerated using manganese sulfate catalyst at the 0.15 $Mn^{++}/S^{=}$ ratio (added in three liquid feeds 15 minutes apart). Aeration of this initial mixture for 1.75 hours reduced the sulfide from 2,620 mg/l to zero for a mean oxidation rate of 41.3 lb $S^{=}$/hr. While this first use of the catalyst gave a lower than expected oxidation rate, reuse of the catalyst-floc in a subsequent run showed that approximately 75% of the catalytic activity was retained. After the first run had been completed, an additional 3,700 gallons of fresh unhairing waste was added to the reaction vessel to bring the sulfide level up to 1,400 mg/l. Without additional catalyst, 2.5 hours of aeration effected a reduction to the zero sulfide level. The mean oxidation rate for this reused catalyst run was 32.8 lb $S^{=}$/hr.

In another full-scale sulfide oxidation run, catalyst was added to a 5,700 gallon batch at the 0.05 $Mn^{++}/S^{=}$ ratio. This first use of catalyst effected a reduction in sulfide from 3,680 mg/l to zero within 3 hours, for a mean oxidation rate of 58.4 lb $S^{=}$/hr. The aerated waste was drained to leave approximately 3,000 gallons in the reaction vessel. Fresh unhairing waste was then added to increase the volume to 6,200 gallons and the sulfide concentration to 1,780 mg/l. Additional manganese sulfate equivalent to a $Mn^{++}/S^{=}$ ratio of 0.05 was added in three liquid feeds 30 minutes apart. This fresh catalyst-refortified reaction mixture required two hours of aeration to achieve a zero sulfide level for a mean oxidation rate of 46.0 lb $S^{=}$/hr. These data suggest, therefore, that while the catalyst floc does indeed retain catalytic activity, reuse of this manganese sludge to augment fresh catalyst, used at the optimum $Mn^{++}/S^{=}$ ratio, does not effect an improvement in oxidation rates. Further investigations into reducing the fresh catalyst feed below the optimum level while augmenting with used catalyst up to the optimum, may further reduce catalyst consumption.

SECTION XIV

RECOVERY OF CRUDE PROTEIN FROM OXIDIZED UNHAIRING WASTE

In cattlehide unhairing, alkali and depilatory agents (usually in the form of lime and sodium sulfide and/or sodium sulfhydrate) are used to solubilize the keratins of the epidermis and hair. The end products of a "hairburn" process include dissolved and colloidal protein as well as suspended fibrous hair fragments, which are transferred to the process effluent. Both dissolved and suspended inorganic salts are also present.

A typical spent unhairing liquor from a hide processor run contained 8,380 mg/l of total Kjeldahl nitrogen, most of which is contributed by the denatured hide proteins. Likewise, the total volatile solids concentration of 51,000 mg/l (of which 30,000 mg/l are volatile suspended solids and 21,000 mg/l are volatile dissolved solids) reflects the extremely high protein decomposition.

Happich et al (65) demonstrated that a recovery scheme employing removal of suspended solids by gravity sedimentation, screening, centrifugation and/or filtration; removal of soluble inorganic compounds by dialysis or ultrafiltration; acidification with acetic acid to pH 5.0 and 3.8; washing and drying; yields a protein fraction of 90 to 92 percent purity.

Approximately 30 percent of the COD (37% BOD) present in the untreated hair-burn waste was separated in the solids fraction after a two-stage centrifugation. Another 31.5 percent of the COD (34.9% BOD) was transferred to the filtrate by ultrafiltration and 38.5% of the COD (28.1% BOD) was actually removed with the protein.

Happich noted that the recovered protein contained the ten "essential" amino acids and closely resembled the composition of native hair. He concluded, however, that the recovered hair protein was low in most of those amino acids relative to whole egg protein and would require supplementation for subsequent use as feed.

To determine the degree of effluent reduction possible through protein recovery from manganese-catalyzed, air-oxidized unhairing wastes, a sample of oxidized waste from an early Pfister & Vogel paddle aeration run was sent to the U.S. Department of Agriculture, Eastern Regional Research Center in Philadelphia for protein recovery by a modified treatment scheme. Precipitation by acidification of the sample, as received at the U.S. Department of Agriculture, to pH 4.2 yielded a tan color protein of 80% purity.

According to Happich, 70% reduction of the COD of the effluent was achieved and 65% of the protein in the effluent was recovered. The product could be purified to 90% protein by re-precipitation. The amino acid composition did not differ significantly from the protein recovered from unoxidized lime-sulfide unhairing effluent.

Another bench-scale experiment was conducted at Pfister & Vogel to further define the conditions for optimum precipitation of protein and subsequent reduction of contaminant levels.

Concentrated hair-burn liquor was air-oxidized using manganese sulfate as the catalyst, at a $Mn^{++}/S^{=}$ ratio of 0.15. After oxidation, the liquor contained approximately 160,000 mg/l of total solids of which 58,400 mg/l was suspended solids.

The titration curve for acidification of (25 ml aliquot) hair-burn liquor with sulfuric acid is shown in Figure 30. The buffering effect of the dissolved protein is evident from the shape of the curve below pH 7.0.

Varying levels of concentrated H_2SO_4, estimated from Figure 30, were added to eighteen 500 ml aliquots of the oxidized waste. The samples were mixed using a Phipps and Bird laboratory stirrer for 5 minutes at 100 rpm followed by 5 minutes of "slow" mixing at 50 rpm. After settling for 60 minutes, the supernatant liquids were decanted and analyzed for pH, total solids and suspended solids. The pH's, which varied from 0.3 to 9.4, were consistently higher than the expected values. This is most likely due to the times elapsed in the precipitation runs contrasted to the 10-15 minutes required for the original titration. While there is no apparent relationship between supernatant pH and suspended solids (supernatant suspended solids concentrations were consistently within the 280-630 mg/l range except at pH 9.4 where a markedly increased level of 1,670 mg/l was observed) the optimum for reduction of total solids, as shown in Figure 31, clearly lies within the 0.9 to 5.0 pH range.

The volumes of the resultant sludges varied from 300 ml to 475 ml as shown in Figure 32, with the minimum lying within the 1.0 to 3.9 pH range. Fortunately, this range of minimum sludge volume is also within the optimum range for precipitation of protein.

At pH 3.2, the supernatant analyzed at 100,200 mg/l of total solids (minimum observed for 18 runs) and 401 mg/l of suspended solids. Thus, approximately 75% of the total solids and 99.7% of the suspended solids present in the original, air-oxidized waste sample were transferred to the 300 ml sludge fraction after precipitation and settling.

Undoubtedly, further sludge dewatering will be required to concentrate these solids which occupied 60% of the original sample volume. Since a portion of the sludge (which contained approximately 80% moisture) dewatered readily by gravity on an 18-mesh screen, dewatering methods recommended for further investigation include gravity screening and sand bed filtration. Lab-scale attempts at vacuum filtration failed to generate a firm cake indicating that conventional rotary vacuum drum filtration is not a feasible

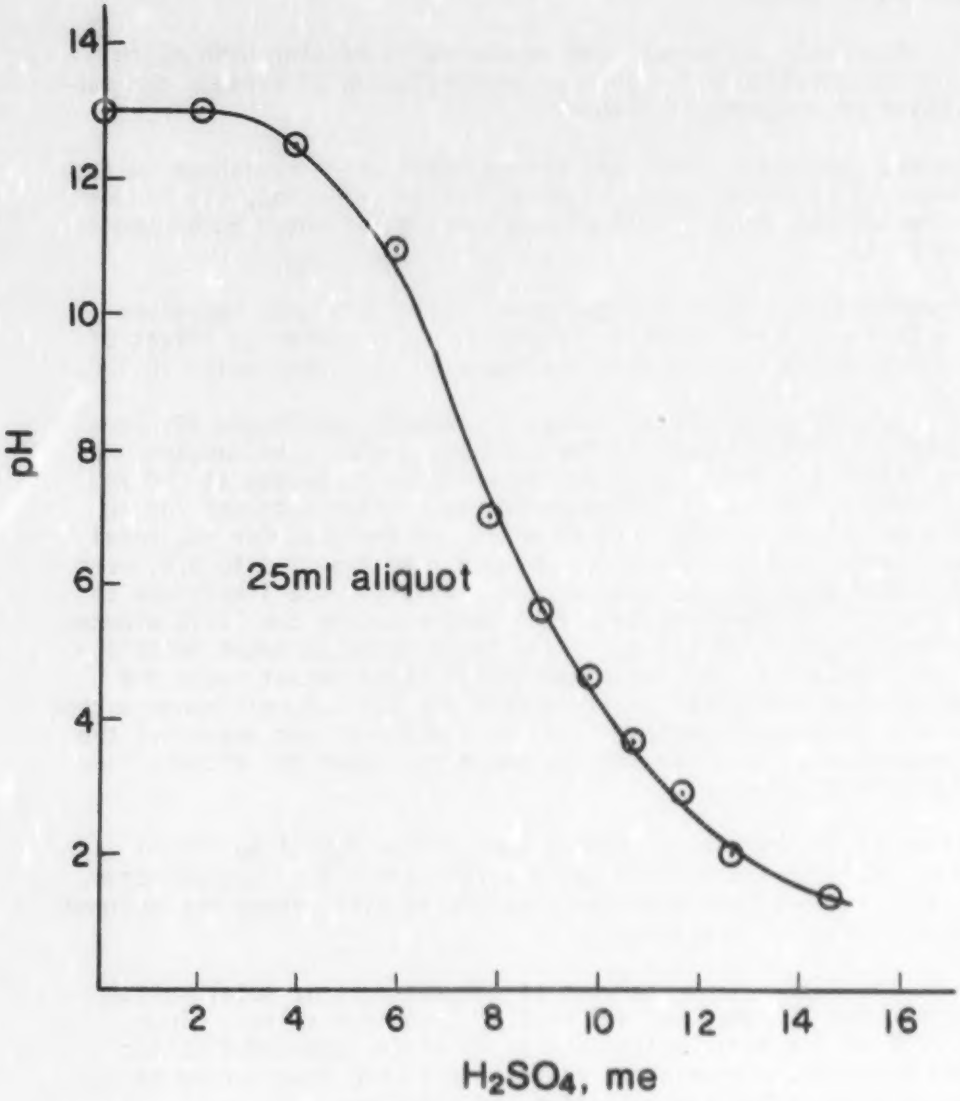

Figure 30: TITRATION CURVE FOR ACIDIFICATION OF OXIDIZED HAIR-BURN LIQUOR.

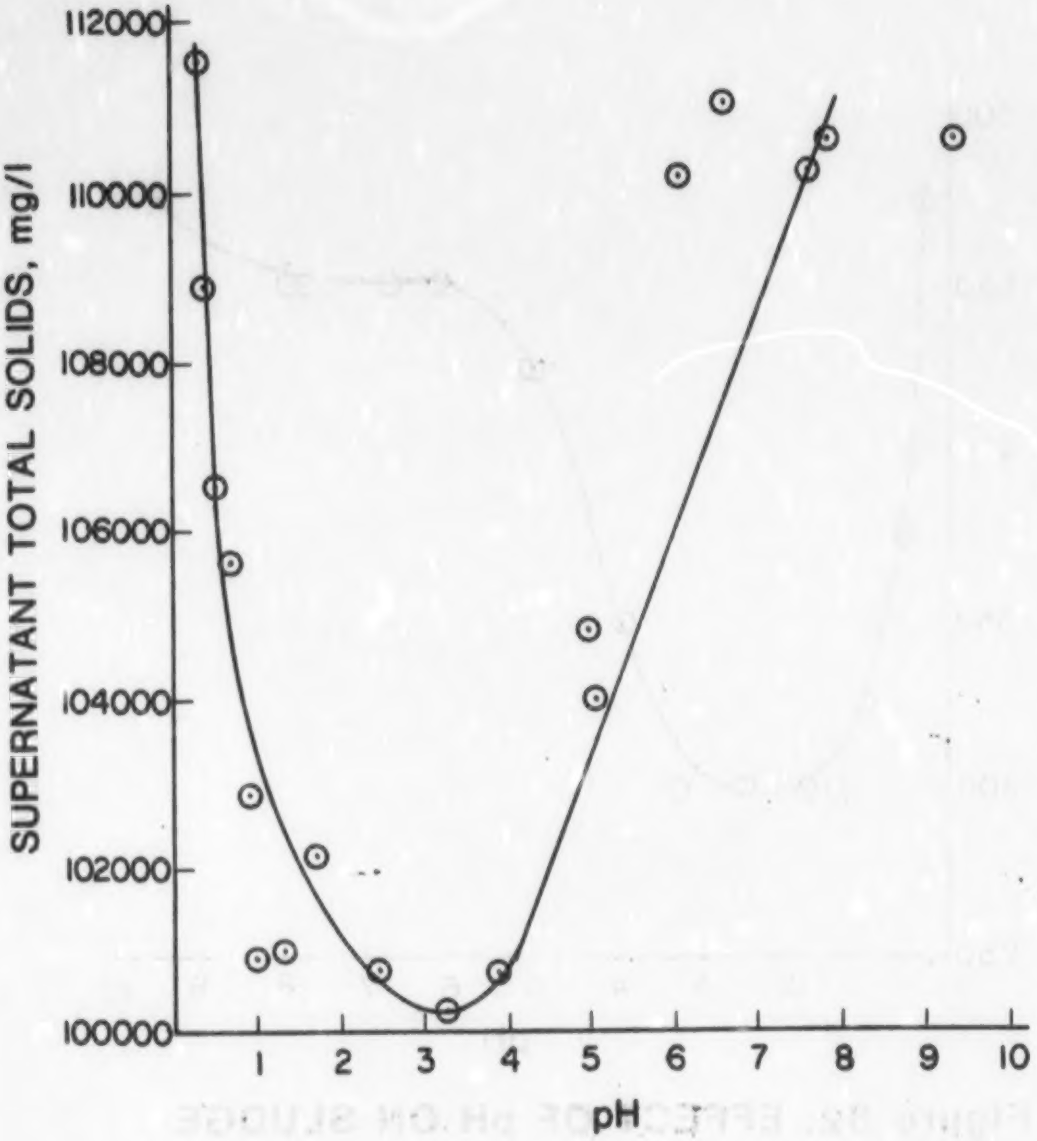

Figure 31: EFFECT OF pH ON TOTAL SOLIDS FOR ACIDIFICATION OF OXIDIZED HAIR-BURN LIQUOR.

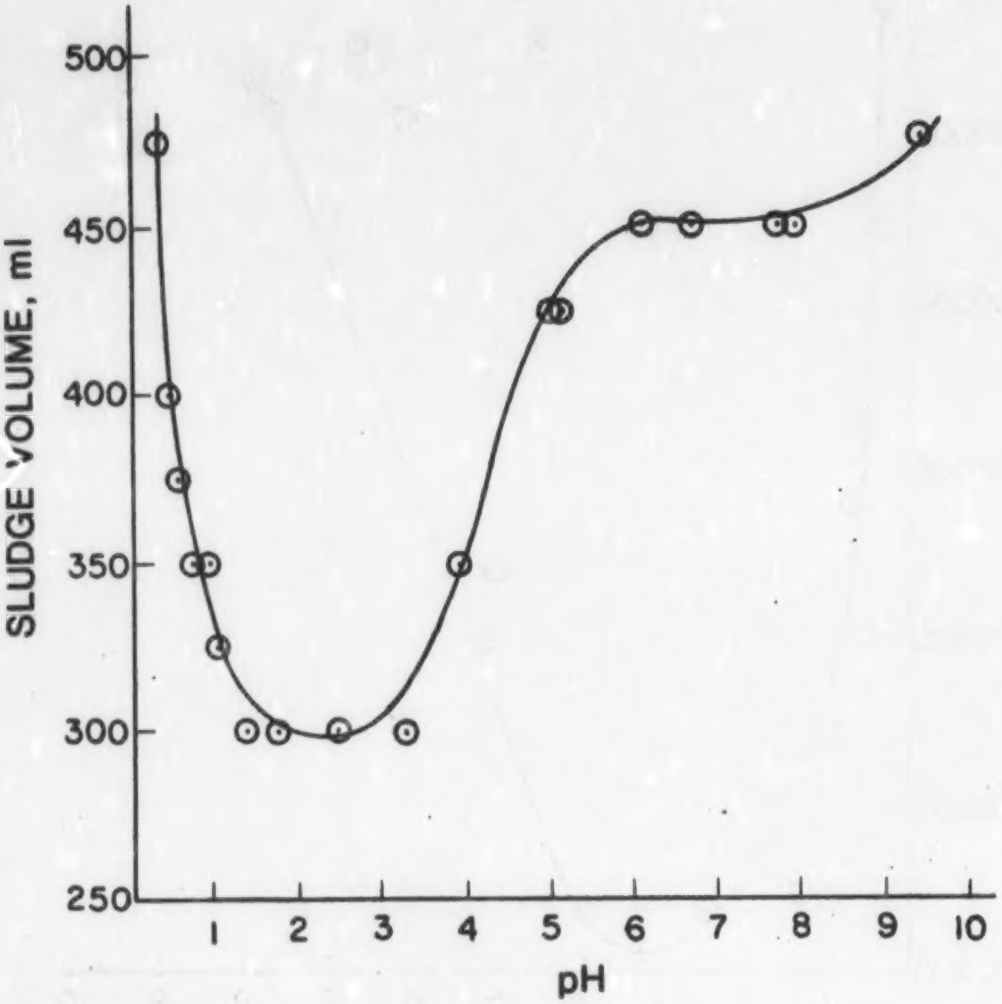

Figure 32: EFFECT OF pH ON SLUDGE VOLUME FOR ACIDIFICATION OF OXIDIZED HAIR-BURN LIQUOR.

alternative.

Another production batch of concentrated unhairing waste was oxidized by the manganese catalyzed air oxidation method until a zero sulfide level was reached. This aerated waste had a pH of 12.0 and contained 156,800 mg/l of total solids, 86,500 mg/l of COD and 7,616 mg/l of Oil and Grease.

Varying amounts of 1:1 sulfuric acid were added to five, 500 ml aliquots of aerated hair-burn waste to reduce the pH to within the 2.4-5.8 range.

As shown in Table 47, after one hour of settling, sludge volumes varied from 275 ml at pH 2.4 to 340 ml at pH 5.3. The sharp decrease in sludge volume at pH 5.8 is indicative of a substantial decrease in the efficiency of protein precipitation. This sludge reduction is consistent with the observed, sharply higher total solids and COD levels in the supernatant at pH 5.8.

The lowest supernatant COD observed was 17,900 mg/l at a pH of 2.4 for a 79.3% reduction over the initial concentration of 86,500 mg/l. Thus, the COD was reapportioned to yield 275 ml of sludge containing approximately 90% of the original COD.

TABLE 47. TREATMENT OF UNHAIRING WASTES BY PROTEIN PRECIPITATION

Sample	pH	Sludge volume, ml	Supernatant TS, mg/l	Supernatant COD, mg/l
1	5.80	280	113,350	31,700
2	5.30	340	107,910	25,100
3	4.00	330	105,610	19,800
4	3.75	330	104,130	19,500
5	2.40	275	103,870	17,900

As indicated in SECTION XII, these concentrated hair-burn liquors comprise only a small fraction of the total wastewater flow (i.e., approximately 11,700 gal hair-burn liquor vs approximately 1.5 million gal total daily flow), yet contribute substantially to pollutant loadings. These concentrated liquors contain an estimated 11% of the total BOD loading, 18% of the total COD and 20% of the suspended solids. When the capture volume is increased from 730 gal to 3,300 gal per hide processor production run, the BOD, COD and suspended solids as a percentage of total effluent loadings are increased to 19%, 33% and 30%, respectively.

Therefore, it appears from these results that precipitation of crude protein from oxidized unhairing wastes can effect significant reductions in total plant loadings provided adequate methods of sludge dewatering and disposal can be demonstrated. Therefore, future R & D efforts should be directed toward sludge handling methods and ultimate sludge utilization, in addition to optimization of this protein recovery pretreatment process through operation of a pilot plant.

SECTION XV

REMOVAL OF SOLIDS FROM SOAK WASTES

Our sampling and analyses of individual process waste fractions reveal that up to 12,000 mg/l of fixed suspended solids have been present in spent soak liquors. Further investigation showed these fixed solids to be largely sand. The soak liquors from four packs of conventionally cured, unfleshed and untrimmed hides were found to contain more sand than any other hide-cure types.

Equilibrated soak liquors from the soaking of various types of hides were sampled and analyzed for acid insoluble ash according to the following technique. An aliquot of the soak liquor (300-1,000 ml) was settled for approximately five minutes and the supernatant was decanted and discarded. The residue was transferred to an evaporating dish, evaporated to dryness and ignited in a muffle furnace for 30 minutes at 550°C. After cooling, the ash was resuspended in 6N hydrochloric acid, boiled to dissolve any metal oxides or carbonates and then diluted with distilled water. The mixture was filtered through ashless filter paper and washed with several aliquots of distilled water. The filter paper containing the residue was then folded and transferred to a weighed evaporating dish and again ignited at 550°C for 30 minutes. The ash content, thus determined, was reported as sand from four hide sources, as follows:

Lot	Cure	lb sand/1000 lb hide
A	Brine cured, unfleshed	1.44
B	Brine cured, fleshed	0.28
C	Conventional cured, fleshed	0.44
D	Conventional cured, unfleshed	3.26
	Average	1.34

Thus, the quantity of sand dislodged from cured hides from four separate hide lots averaged 1.34 lb/1000 lb hide, ranging from a minimum of 0.28 lb/1000 lb hide for a lot of brine cured, fleshed and trimmed hides to 3.26 lb/1000 lb hide for a lot of conventionally cured, unfleshed hides.

In the design of most conventional municipal wastewater treatment facilities, grit chambers remove inert substances preventing wear of pumps and machinery and reducing accumulation in treatment units. Most grit chambers are installed to remove sand and other dense particles with a specific gravity of 2.65 or greater and with a minimum diameter of 2×10^{-2} cm (66).

Likewise, collection systems are designed to maintain minimum transport velocities of 2.0-3.0 fps (67) to maintain these particles in suspension.

A sieve analysis of a portion of sand collected from the soak liquors of a typical lot of conventionally cured, unfleshed hides yielded the results shown in Table 48. As these data indicate, nearly 80% of the particles (weight basis) lie within the 0.074-0.297 mm diameter range. Also, only slightly more than 53% of this sand would be expected to settle out in a typical grit chamber.

Since wet sand slurry is approximately 40% water by volume (specific gravity of the mixture is thus estimated to be 1.99) approximately 159 pounds of sand would generate one cubic foot of wet grit. Thus, at the average sand discharge level from soaking, approximately 0.0065 ft^3 of grit per 1000 pounds hide is generated. At a mean total tannery effluent flow of 6,590 gal/1000 lb hide, this is equivalent to only one cubic foot of grit per million gallons--less than one-quarter the amount of grit recovered from the "average" municipal treatment facility per million gallons treated (68).

TABLE 48. SIEVE ANALYSIS OF SAND FROM SOAK LIQUOR

Mesh Number	Millimeters	% of total weight	Cumulative % of total weight
20	0.84	7.8	7.8
20-30	0.84 - 0.59	5.7	13.5
30-40	0.59 - 0.42	4.0	17.5
40-50	0.42 - 0.297	21.0	38.5
50-70	0.297-0.210	15.1	53.6
70-100	0.210-0.149	17.1	70.7
100-140	0.149-0.105	14.2	84.9
140-200	0.105-0.074	10.4	95.3
200-270	0.074-0.053	3.6	98.9
270	0.053	1.1	100.0

A probe into the separation of sand from these wastes has shown, at least qualitatively, that hydrocyclonic separation is an effective and compact means of treatment. In one trial run, unscreened soak wastes were fed to a hydrocyclonic separator at approximately 20 gpm under a pressure of 50 psi. With an orifice diameter of 1/8", approximately 5% of the influent was recovered as sludge. Visual inspection of the clarified liquor revealed no trace of settleable grit. Thus, where removal of grit before discharge to plant or municipal sewers is desirable, hydrocyclonic separation should be further investigated as a space efficient (but power intensive) alternative to settling.

Further investigation into the treatment of soak liquors was directed at screening as a preparatory step required for recycle of this waste fraction. While a 300^0 pressure screen proved to be impractical because of repeated clogging of the orifices (even at the largest orifice setting), separation of hair and other coarse suspended solids by gravity screening was highly effective. Removal of these solids prior to recycle is necessary to prevent the clogging of process recirculating pumps and the resulting intolerable production delays.

Approximately 700 gallons of soak wastes from a single production run were pumped over an 18" wide gravity screen with 0.040" openings at a mean rate of 130 gpm.

At a throughput rate of 7.2 gal/min per inch of screen width all visible traces of flesh and hair as well as a portion of the sand were removed. Approximately eight gallons of sludge were recovered with no significant blinding of the screen. After the sludge supernatant was decanted and screened a second time, 39 pounds of wet solids were recovered.

Further work to optimize the solids removal/screen opening (and thus feed rate) relationship is indeed warranted where soak liquor pretreatment or recycle is desired.

SECTION XVI

GENERATION OF OIL & GREASE AND CHROME DURING BLUE STOCK WRINGING

Substantial quantities of Oil and Grease and total chromium are extracted from the tanned sides during the wringing process. Blue stock leather analyses and weight data before and after wringing indicate that this mechanical extraction of Oil and Grease is equivalent to approximately 10% of Pfister & Vogel's total tannery effluent loading. Likewise, total chromium equivalent to approximately 13% of the total tannery effluent loading is extracted from the blue stock during wringing.

Four packs of brine-cured hides from a single hide lot, which had been fleshed and trimmed by the packer after curing, were processed to the blue condition in a hide processor. After tanning, the sides were piled for 16 hours, weighed, wrung and then reweighed. Adjacent cuttings before and after wringing were taken from the shoulder, kidney and belly of 12 sides (6 rights and 6 lefts) selected at random. The relative position of the adjacent cuttings was alternated over the 12 sides. Two 2" x 1" pieces were taken from each cutting. One set of pieces was immediately analyzed for moisture content while the second set was dried overnight at room temperature and subsequently ground and composited to yield six representative leather samples. Analysis of the samples according to standard ALCA methods yielded the data shown in Table 49.

The average fat content before wringing was 1.37% while after wringing fats decreased to 1.33% on an "as received" basis. Average chromic oxide content increased however from 1.32% Cr_2O_3 before to 1.53% after wringing.

As Table 50 shows, the average weight of a side of blue stock decreased 20.9% from 24.58 lb before to 19.44 lb after wringing while the equivalent weight of a cured side charged to the tanning process averaged 21.99 lb.

The mass-balance analysis of blue stock wringing shown indicates that wringing extracts approximately 3.55 pounds of fats and 0.813 lb Cr (1.19 lb Cr_2O_3) per 1000 pounds of cured hide charged to the process. This is equivalent to 10.4% and 13.1% of our mean total tannery loadings of Oils and Greases and total chromium respectively of 34.1 lb/1000 lb and 6.20 lb/1000 lb (based on actual raw-material mix).

TABLE 49. EFFECT OF WRINGING ON BLUE STOCK ANALYSIS

	Belly	Shoulder	Kidney	Average
% Moisture				
before wringing	72.17	64.67	61.48	66.12
after wringing	63.16	59.30	56.28	59.58
% Solids				
before wringing	27.83	35.33	38.52	33.89
after wringing	36.84	40.70	43.72	40.42
% Fats - as received				
before wringing	1.47	0.60	2.05	1.37
after wringing	1.20	0.60	2.19	1.33
% Fats - moisture free				
before wringing	5.30	1.70	5.33	4.11
after wringing	3.26	1.47	5.00	3.24
% Cr_2O_3 - as received				
before wringing	1.072	1.414	1.467	1.317
after wringing	1.356	1.585	1.651	1.531
% Cr_2O_3 - moisture free				
before wringing	3.852	4.002	3.808	3.887
after wringing	3.681	4.302	3.776	3.920

TABLE 50. CHROME & FATS DISCHARGED FROM BLUE STOCK WRINGING

	Fats	Cr_2O_3
Blue stock		
before wringing, lb/side	0.3367	0.3237
after wringing, lb/side	0.2586	0.2976
Discharged		
lb/side	0.0781	0.0261
lb/1000 lb cured hide	3.55	1.10

Cured weight of stock = 21.99 lb/side

Blue stock weight before wringing = 24.58 lb/side

Blue stock weight after wringing = 19.44 lb/side

SECTION XVII

GRAVITY SEPARATION OF OIL & GREASE FROM BEAMHOUSE WASTES

Of the several wastewater pollutants which characterize tannery effluents, Oil and Grease is perhaps the most ubiquitous. It is generated (or released) during practically every step of the "lower tannery" leathermaking processes, which contribute approximately 85% of the total tannery Oil and Grease loadings. In fact, the Oil and Grease load in the waste fractions from soaking, liming, reliming, bating and tanning each individually exceeds the promulgated EPA effluent standard (recently rescinded) for the direct discharge of Oil and Grease. Soaking, for example, contributes approximately 7.5 lb of Oil and Grease per 1000 lb of cured hide charged to the process--ten times the EPA guideline for total tannery waste (0.75 lb/1000 lb). Even pickling wastes, which alone contribute 0.44 lb Oil & Grease/1000 lb hide, are discharged at a concentration more than 100 times the allowed total effluent Oil and Grease concentration of 15 mg/l (at the EPA design flow of 6 gal/ lb hide). Thus, to achieve substantial reductions in total effluent Oil and Grease loadings every "lower tannery" wastewater fraction requires treatment; and to meet the EPA guidelines, 97.8% of all Oil and Grease must be removed (from 34 lb/1000 lb to 0.75 lb/1000 lb).

To this end, lab-scale experiments were conducted to determine the treatability of segregated waste fractions by gravity separation or "simple flotation." Samples of six different lower tannery process waste streams were transferred to one liter graduated cylinders.

Each sample was thoroughly mixed and an aliquot was withdrawn to determine the initial Oil and Grease content of the raw waste. After one hour of separation under quiescent conditions, another aliquot was withdrawn midway between the supernatant and sludge layers and analyzed for Oil and Grease.

As Table 51 shows, the pickle and spent chrome samples initially contained 2,467 mg/l and 3,524 mg/l of Oil and Grease respectively at corresponding pHs of 2.63 and 3.45. These Oil and Grease fractions which are primarily insoluble fatty esters and fatty acids, float readily and concentrate in the scum layers. The clarified interlayers analyzed at 272 mg/l and 428 mg/l respectively indicating a substantial redistribution of the Oil and Grease component. Thus, under ideal conditions, reductions of 89.0% and 95.0% of the Oil and Grease in pickle liquors and spent chrome liquors by "simple flotation" have been observed.

The soak liquor sample contained 6,333 mg/l of Oil and Grease at a pH of 9.72. After settling, the interlayer contained 6,062 mg/l indicating that the Oil and Grease must be present in the waste fraction as emulsions and/or as soluble soaps. Likewise, no substantial reduction was noted in the slightly alkaline bate liquor sample which had an 8.3 pH.

A pronounced redistribution of Oil and Grease (probably as calcium soaps) was observed in the hair-burn liquor. The combined scum and sludge fractions, however, equalled 75% of the original volume, making gravity separation impracticable for the "removal" of Oil and Grease.

In the relime liquor sample also, a substantial volume of sludge was generated while a reduction in Oil and Grease from 1,010 mg/l to 134 mg/l in the clarified interlayer was observed.

As these results suggest, the naturally-occurring Oil and Grease (introduced by the hides) in several isolated "lower tannery" waste fractions disproportionate between the sludge and scum layers and the clarified interlayers by gravity alone. Most notably, substantial reductions in Oil and Grease are predicted for the "simple flotation" of spent pickle and spent chrome liquors using surface skimming for scum removal. More advanced flotation techniques such as dissolved air flotation, dispersed air flotation and foam fractionation should be investigated as means of further improving Oil and Grease separation from these two waste fractions.

The results for lime and relime liquors suggest that substantial Oil and Grease reductions are not practicable using simple flotation techniques, but might only be made feasible in conjunction with the removal of major quantities of suspended solids followed by sludge dewatering and final disposal.

While bate liquors are not amenable to substantial reductions by simple flotation, additional research needs to be carried out to determine whether chemical additives such as polyelectrolytes and/or acid neutralization can "free" the Oil and Grease for separation.

Similarly, acid addition to soak liquors reprecipitates stabilized or dissolved Oil and Grease to induce separation. For that purpose, spent pickle liquor was added to several soak liquor aliquots at pickle-to-soak volume ratios varying from 1:1 to 2.25:1.

The pickle-soak mixtures were transferred to graduated cylinders and settled under quiescent conditions. As Table 52 shows, the clarified interlayer after one hour analyzed at 256 mg/l, 414 mg/l and 2,320 mg/l for pickle-to-soak ratios of 1:1, 1.35:1 and 2.25:1, respectively.

The maximum degree of redistribution of the Oil and Grease was thus observed at the 1:1 ratio and at an initial pH of 7.9. The final pH was 8.5. The addition of pickle liquor to the soak liquor followed by a short period of gentle stirring produced a large, sturdy, flotable floc. After one hour the floc particles developed into a scum layer equivalent to 390 ml/l, while the volume of solids settling to the bottom was negligible. Thus, while a 94.3% reduction of Oil and Grease in the interlayer (from 4,515 mg/l to 256 mg/l) was observed, the voluminous scum which generated would surely require further dewatering. Dissolved air flotation of this material should be investigated as an alternate, probable means of improving scum concentrations.

TABLE 51. EFFECT OF FLOTATION ON THE OIL & GREASE CONTENT OF VARIOUS WASTE FRACTIONS

Waste fraction	Raw Waste			Clarified interlayer
	pH	Settlable solids, ml/l	Oil & Grease, mg/l	Oil & Grease, mg/l
Soak	9.72	4	6,333	6,062
Lime	12.28	600	11,260	896
Relime	12.40	60	1,010	134
Bate	8.30	19	724	522
Pickle	2.63	30	2,467	272
Spent Chrome	3.45	0.3	8,524	428

TABLE 52. FLOTATION OF PICKLE/SOAK WASTEWATER MIXTURES

Pickle/Soak Ratio	pH		Oil & Grease, mg/l		Settlable solids, ml/l	Flotable solids, ml/l
	Before flotation	After flotation	Before flotation	After flotation		
1.0	7.9	8.5	4,515	256	0.9	390
1.35	7.1	8.3	4,020	414	0.8	230
2.25	6.0	7.3	3,510	2,320	-	140

SECTION XVIII

RECOVERY OF LIME FROM SPENT LIME LIQUORS

A mass-balance analysis of Pfister & Vogel's tannery operations indicates that the sum of the waste water suspended solids loadings from the individual process steps of soaking, liming, bating, pickling and tanning plus the loading from retanning, coloring, fatliquoring and subsequent "upper tannery" operations equals only 60% of the suspended solids loadings as determined from the analysis of 24-hour total effluent composite samples (flow proportional) and total effluent flow data. These data demonstrate that the combination of individual subprocess wastes in equalization/neutralization basins or ponds will create a substantial increase in the suspended solids content. Most significantly, the presence of lime-bearing fractions will bring about the following solids-producing interactions: they will react with spent chrome wastes to yield chromium hydroxide. The carbonates from other processing steps combine with free calcium hydroxide to yield sparingly soluble calcium carbonate. Likewise, the formation of insoluble calcium soaps is expected. Finally, the divalent calcium ions act as a coagulant to destabilize any colloidal solids present. Thus, the reduction of lime wastes from tannery effluents by lime liquor recycle is expected to reduce total effluent suspended solids loadings well beyond the levels predicted by the mass balance contribution of the lime alone.

Preliminary investigations suggest that one possible recycle scheme is the collection and concentration of spent lime liquors by flocculent settling followed by refortification to produce a "stock" lime slurry for re-use. A second alternative investigated was process modification to reduce relime float volumes allowing direct reuse of a major fraction of the lime-concentrate in subsequent unhairing or reliming runs.

Two matched sides leather tests in hide processors were conducted to determine the more practical recycle "fit" for spent lime liquors in our leather-making process. In the first test, the relime float was drained halfway through the relime, then followed by a sequential fresh water flood and run. In the control runs, the relime float was retained such that after the fresh water flood, the float volume was approximately twice the volume of the test lime-concentrate drain. Analysis of the lime waste waters showed that the first test drain contained alkalinity equivalent to 93 lb $Ca(OH)_2$, with the final drain after flooding containing an additional 85 lb $Ca(OH)_2$. The relime drain from the regular hide processor contained alkalinity equivalent to 193 lb of $Ca(OH)_2$. Therefore, as the data shows, the intended concentration of lime by process modification was not forthcoming. In the test hide processor run the initial drain contained only 52% of the combined alkalinity of the two test drains. Likewise, the initial test drain contained only 48% of the lime in the control run drain, and at 18,000 mg/l alkalinity (as $Ca(OH)_2$) there was no significant difference in concentration over the control.

In the first test, the finished leather showed the test sides to be considerably smoother and better for fat wrinkles, finish break and hair cell than the controls. However, they were substantially looser and somewhat firmer than the control sides. There was no difference in thickness, in wooliness of the flesh, or the veininess of the sides. Also, the physical strength of the test sides as measured by Satra grain burst force, Satra extension and two-hole stitch tear was equal to the control sides.

In a repeat of the test, the test sides remained slightly better for smoothness, fat wrinkles, finish break and hair cell and this time were equal to the controls for tightness, softness and veininess with an improvement in the flesh noted.

In the second test, a substantial improvement in physical strength of the test sides was observed. Satra grain burst force averaged 68 kg vs 61 kg for the controls. The corresponding increase in extension was from 8.71 mm to 8.90 mm. Likewise, stitch tear strength increased from 91 pounds to 100 pounds.

Since these results suggest that process float volume and drain modifications do not effect any concentration of contained alkalinity, alternative measures including collection and thickening by sedimentation or hydrocyclonic separation were investigated.

In one probe experiment, 800 gallons of spent lime liquor containing 17,680 mg/l of suspended solids and 17,800 mg/l alkalinity as $Ca(OH)_2$ were collected from a single hide processor. This waste was pumped at a rate of 37.5 gpm to a pair of hydrocyclonic separators having orifice diameters of 3/16". The sludge which was generated at 4.0 gpm contained 52,750 mg/l of suspended solids and 40,000 mg/l of lime.

Thus, approximately 25% of the contained alkalinity of the cyclone supernatant and sludge was concentrated in the sludge fraction which equaled 10.6% of the original feed volume. The remaining 75% of the alkalinity, however, was discharged in the supernatant which was equivalent to 89.4% of the feed volume. Likewise, approximately 30% of the combined suspended solids was separated in the sludge, and 70% remained in the supernatant. Therefore, even within the constraints of the fixed orifice diameter and feed pressure available for this experiment, a significant disproportionation of alkalinity and solids between the cyclone supernatant and sludge has been effected. Further optimization of the operating conditions for hydrocyclonic separation of lime from spent lime liquors should improve recovery efficiencies and, indeed, merits further investigation.

In another pilot-scale experiment 620 gallons of spent relime liquor containing 18,100 mg/l alkalinity as $Ca(OH)_2$ was collected from a typical production run. A 500 ml aliquot of the waste was transferred to a graduated

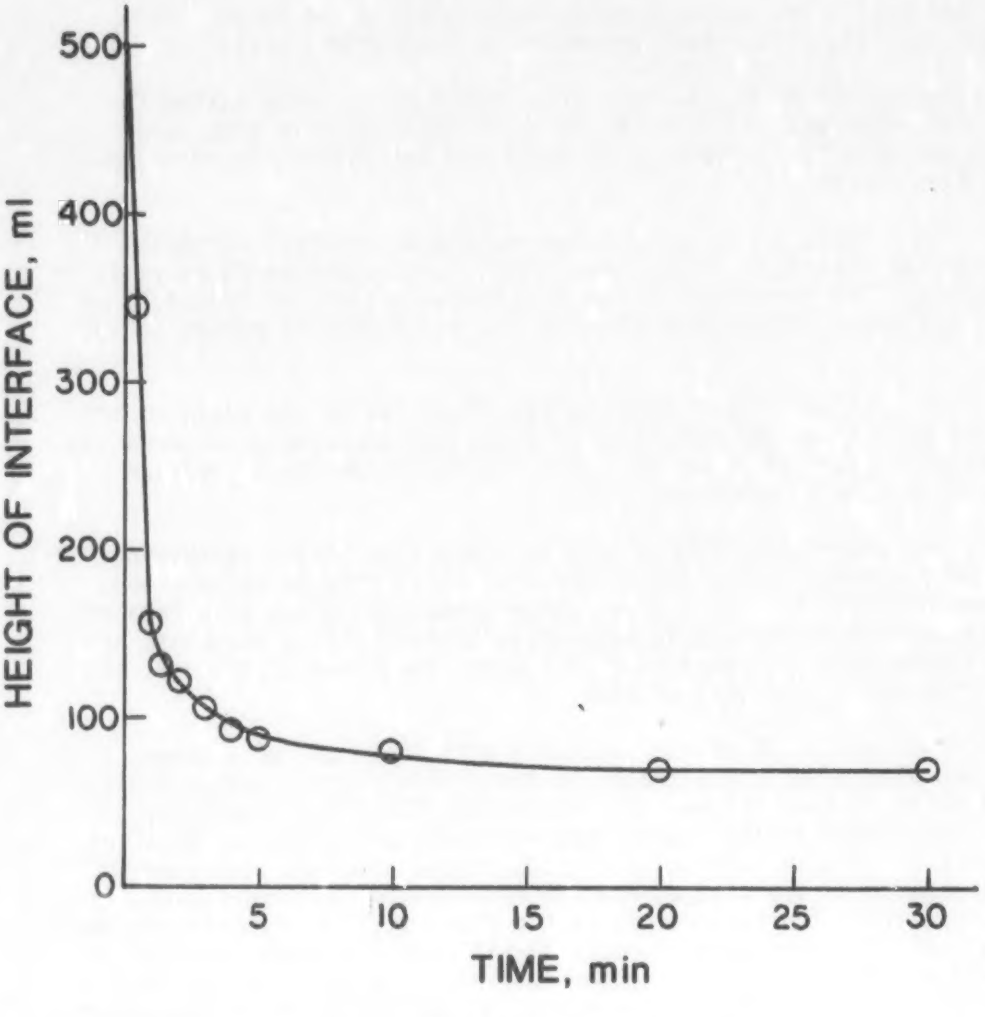

Figure 33: FLOCCULENT SETTLING OF LIME IN RELIME LIQUOR.

cylinder and treated with 100 ppm of an anionic polyelectrolyte (Rohm & Haas Primafloc A-10). After one minute of rapid mixing followed by five minutes slow mixing the suspension was left to settle under quiescent conditions. The settling curve shown in Figure 33 demonstrates the rapid-settling characteristics of the resultant flocculent mixture. After two hours an aliquot of the supernatant was withdrawn and analyzed at 5,840 mg/l $Ca(OH)_2$ for a 67.7% reduction. A sludge volume of 60 ml was recorded, and by mass-balance calculations was estimated to contain 109,000 mg/l of $Ca(OH)_2$.

Subsequently, 100 ppm of Primafloc A-10 was added to the 620 gallon batch, the mixture was agitated gently for 5 minutes, and then settled for two hours. The first 50 gallons of thickened sludge was drawn off from the bottom of the conical settling tank. This sludge analyzed at 101,000 mg/l of $Ca(OH)_2$ alkalinity equivalent to 42 pounds of lime. The supernatant contained 5,900 mg/l $Ca(OH)_2$ for a reduction of 67.4%. While approximately 45% of the lime was actually recovered, mass-balance analysis indicates that as much as 77% might be removed in continuous steady state operation.

These results demonstrate that a better than five-fold concentration of alkalinity in spent relime liquors is possible, thus making recycle by fortification with powdered hydrated lime and subsequent reuse in unhairing-liming production steps at least possible from a mass-balance standpoint. Of course the most important consideration - the effect of such a recycle scheme on leather quality remains to be determined.

SECTION XIX

ACKNOWLEDGMENTS

This study was conducted by the Pfister & Vogel Tanning Company at Milwaukee, Wisconsin under the direction of Dr. James W. Constantin, Vice President, Research and Development. George B. Stockman served as Project Engineer.

Dr. J. David Eye, Professor of Environmental Health Engineering at the University of Cincinnati served as consultant to Pfister & Vogel Tanning Company during the project. Robert Fulton, Plant Engineer and Robert Kusserow, Chief Engineer for Pfister & Vogel, assisted during the construction phase of the project.

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SECTION XX

REFERENCES

1. U.S. Environmental Protection Agency. Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Leather Tanning and Finishing Point Source Category. Washington, D.C. EPA 44/1-73/015. November 1973. p.1.

2. Harnly, J.W. Journal of the American Leather Chemists Association, 46:169, 1951.

3. Benrud, N.C. Journal of the American Leather Chemists Association, 46:171, 1951.

4. Miller, H. Report of the Symposium on Industrial Waste of the Tanning Industry. Journal of the American Leather Chemists Association, Supplement No. 15:25, 1970.

5. Davis, M.H. and J.G. Scroggie. Investigation of Commercial Chrome-Tanning Systems, Part III. Journal of the Society of Leather Technologists and Chemists, 57:53-58, 1973.

6. Davis, M.H. and J.G. Scroggie. Investigation of Commercial Chrome-Tanning Systems, Part II. Journal of the Society of Leather Technologists and Chemists, 57:35-38, 1973.

7. Petruschke, R. A Study of Chrome Recovery from Spent Chrome Tanning Liquors. M.S. Thesis, University of Cincinnati, 1959.

8. Hauck, R.A. Report on Methods of Chromium Recovery and Reuse From Spent Chrome Tan Liquor. Journal of the American Leather Chemists Association, 67:422, 1972.

9. Young, H.H. Effluent Treatment for a Small Tannery. Journal of the American Leather Chemists Association, 68:308, 1973.

10. Weber, W. Report of IULCS Effluent Commission. Journal of the Society of Leather Technologists and Chemists, 57:63, 1973.

11. Das, B.M., J.K. De and S.N. Bose. Recovery of Chromium from Waste Chrome Liquors. Bulletin of the Central Leather Research Institute, Madras, 1(5):14, 1954.

12. Abramovich, A. The Separation of Chromium from Tannery Effluents. Izvest. Vysshikh Ucheb. Zavedenii, Technol. Legkoi Prom., No. 3:36041. From C.A., Vol. 56, No. 7068i.

13. Bianchi, A. French Patent No. 1,113,962, April 6, 1956. From C.A., Vol. 53, No. 9708g.

14. Hognes, T.R., W.C. Johnson and A.A. Armstrong. Qualitative Analysis and Chemical Equilibrium. Holt, Rinehard and Wilson, Inc., Chicago, 1966. p.565.

15. Sawyer, C.N. and P.L. McCarty. Chemistry for Sanitary Engineers. McGraw-Hill Company, St. Louis, 1967. p.220.

16. Metcalf and Eddy, Inc. Wastewater Engineering: Collection, Treatment, Disposal. McGraw-Hill Book Company, New York, 1972. p.296.

17. Anon. Waste Water Treatment with Air Flotation. Environmental Science and Technology, 7(11):916, 1973.

18. Eckenfelder, W.W. Jr. and D.J. O'Connor. Biological Waste Treatment. Pergamon Press, New York, 1961. p. 182.

19. Bhattacharyya, D., J.A. Carlton and R.B. Grieves. Continuous Precipitate Flotation of Chromium (III) Hydroxide. American Institute of Chemical Engineers Journal, 17:419, 1971.

20. Rich, L.G. Unit Operations of Sanitary Engineering. John Wiley and Sons, Inc., Clemson, S.C., 1971. p.93.

21. ibid. p.167.

22. The Bauer Brothers Company. Bulletin G-422. Springfield, Ohio, 1969.

23. Orthman, A.C. Tanning Processes. Hide and Leather Publishing Co., 1945. p.374.

24. ibid. p.376.

25. American Mutual Insurance Alliance. Handbook of Hazardous Materials. Technical Guide No. 7. Chicago, IL, 1974. p.60.

26. U.S. Environmental Protection Agency, Technology Transfer. Process Design Manual For Sulfide Control in Sanitary Sewerage Systems. 1974, p.2.2.

27. ibid. p.2.6.

28. ibid. p.2.3.

29. Bailey, D.A. IULCS Tannery Wastes Commission, Minutes of the Fifth Meeting of the Commission in Barcelona. Journal of the Society of Leather Technologists and Chemists, 58(1):3, Jan.-Feb. 1974.

30. van Vlimmeren, P.J. Tannery Effluent. Journal of the American Leather Chemists Association, 67:392-393, 1972.

31. A.C. Lawrence Leather Company. Activated Sludge Treatment of Chrome Tannery Wastes. Federal Water Pollution Control Administration, Department of the Interior, Washington, D.C., Sept. 1969. p.135.

32. op. cit. Bailey. p.3.

33. ibid.

34. U.S. Environmental Protection Agency, Office of Water Program Operations. Pretreatment of Pollutants Introduced into Publicly Owned Treatment Works. Washington, D.C., October 1973. p.C-4.

35. Baily, D.A. Tannery Effluent Report to the Members of the Effluent Commission of the International Union of Leather Chemists Societies. Journal of the Society of Leather Trades Chemists, 56:52, 1972.

36. ibid. p.53.

37. op. cit. van Vlimmeren. pp. 397-399.

38. Eye, J.D. and D.P. Clement. Oxidation of Sulfides in Tannery Waste Waters. Journal of the American Leather Chemists Association, 67:256-267, June 1972.

39. Chen, K.Y. and C.J. Morris. Oxidation of Sulfide by O_2: Catalysis and Inhibition. Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineers, 98(SA1):215-227, Feb. 1972.

40. Krebs, H.A. Uber die Wirkung der Schwermetalle aus die Autoxydation der Alkalisulfide Und des Schwefelwasser-stoffs. Biochim. Z., 204:343, 1929. From: Chen, K.Y. and C.J. Morris. Oxidation of Sulfide by O_2: Catalysis and Inhibition. Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineers, 98(SA1):226, Feb. 1972.

41. Bailey, D.A. IULCS Effluent Commission, Fourth Meeting of the Commission in Lyon. Journal of the Society of Leather Technologists and Chemists, 57:64, 1973.

42. Black, A.P. and J.B. Goodson, Jr. The Oxidation of Sulfides by Chlorine in Dilute Aqueous Solutions. Journal of the American Water Works Association, 44:309-316, April 1952.

43. Skoog, D.A. and D.M. West. Fundamentals of Analytical Chemistry, 2nd Ed. Holt, Rinehart and Winston, Inc., Chicago, 1969. pp. 445-465.

44. Chen, K.Y. and J.C. Morris. Kinetics of Oxidation of Aqueous Sulfide by O_2. Environmental Science and Technology, Easton, PA, 6:534. June 1972.

45. ibid. p.530.

46. op. cit. Chen and Morris. Oxidation of Sulfide by O_2. pp. 217-218.

47. Fair, G.M., J.C. Geyer and D.A. Okun. Water and Wastewater Engineering, Vol. 2. John Wiley and Sons, Inc., New York, N.Y., 1968. p.35.24.

48. op. cit. Eye and Clement. p.260.

49. ibid. p. 259.

50. op. cit. Sawyer and McCarty. pp. 383-393.

51. APHA, AWWA and WPCF. Standard Methods for the Examination of Water and Wastewater, 13th Ed. American Public Health Association, Washington, D.C. 1971. pp. 474-488.

52. Aqua-Aerobic Systems, Inc. Engineering Manual. Rockford, IL. p. 5.4.

53. Stewart, R. Oxidation by Permanganate. Reprinted from: Oxidation in Organic Chemistry, Part A, K.B. Wiberg, ed. Academic Press, New York, 1965. p. 28.

54. op. cit. U.S.E.P.A. Process Design Manual for Sulfide Control in Sanitary Sewerage Systems. pp. 5.37-5.41.

55. ibid. p. 5.31.

56. op. cit. Black and Goodson. p. 310.

57. op. cit. U.S.E.P.A. Process Design Manual for Sulfide Control in Sanitary Sewerage Systems. pp. 5.31-5.32.

58. op. cit. Fair, Geyer and Okun, Vol. 2. p. 31.14.

59. Environmental Control Group. How Much Air? Rex Chainbelt Inc., Waukesha, Wisconsin. 7 pp.

60. Environmental Control Group. Air Lock Crown Diffuser. Rex Chainbelt Inc. Bulletin AEP-398, 1970.

61. op. cit. Fair, Geyer and Okun. Vol. 2, p. 25.24.

62. Spencer Turbine Company. Spencer Turbo-Compressors. Bulletin 126J, Hartford. p. 16.

63. Envirotech Corporation, Eimco Processing Machinery Division. Eimco MS-8. Salt Lake City.

64. op. cit. Aqua-Aerobic Systems, Inc. p. 1.10.

65. Happich, W.F., M.L. Happich, J.E. Cooper, S.H. Feairheller, M.M. Taylor, D. Bailey, H.W. Jones, E.F. Mellon and J. Naghski. Recovery of Proteins from Lime-Sulfide Unhairing Effluents. Eastern Regional Research Laboratory, Agriculture Research Service, U.S. Department of Agriculture, Philadelphia, PA. Presented in part at the sixty-eighth Annual Meeting of the American Leather Chemists Association, Pocono Manor, PA, June 18-21, 1972.

66. op. cit. Fair, Geyer and Okun, Vol. 2. p. 25.26.

67. Fair, G.M., J.C. Geyer and D.A. Okun. Water and Wastewater Engineering, Vol. 1. John Wiley and Sons, Inc., New York, N.Y., 1966. p. 3.12.

68. op. cit. Fair, Geyer and Okun, Vol. 2, p. 25.29.

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16. ABSTRACT

Reduction of tannery waste, i.e., trivalent chromium, sulfide and oil and grease components has been accomplished by process change. Protein recovery and hydroclonic separation of solids was shown to be possible in tannery processing in reducing waste loading. All waste load reduction was accomplished without loss of leather quality. Waste characterization through material balance was accomplished. Chemical reactions and engineering design factors provide guidance for other plant scale operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

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